METAL-ORGANIC COMPOUNDS

A collection of papers comprising the Symposium on Metal-Organic Compounds, presented before the Division of Industrial and Engineering Chemistry at the 131st National Meeting of the American Chemical Society, Miami, Florida, April 1957.

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Introduction

The papers presented in this volume represent contributions to the first American Chemical Society symposium devoted to the increasingly important area of metal-organic compounds. The term metal-organic has been used to cover broadly those compounds with metal-carbon bonds (usually known as organometallic compounds), as well as the metal-oxygen-carbon compounds (the alkoxides or alcoholates), and the coordination compounds of metals and organic molecules.

This area of metal-organic compounds has already attained immense commercial stature through lead antiknock agents, tin stabilizers for vinyl plastics, and silicon-containing polymers. It shows promise of rather phenomenal future growth in the form of boron-based high energy fuels and aluminum alkyls for olefin-polymerization catalysts. As the knowledge of molecular architecture improves, the combination of metals with organic molecules seems to offer possible solutions to many problems in metal extraction and purification, in formulation of heat-resistant polymers, in propellant systems, surface coatings, agricultural chemicals, and chemical synthesis.

The author's particular interest in this field, which prompted the organization of this symposium, is an interest in the alkali metals—in sodium through his former connection with the Ethyl Corp. and in lithium through his connection with the American Lithium Institute. The alkali metals play a role of dual importance in the field of metal-organic compounds, because the alkali-metal-organics are significant compounds in their own right in organic synthesis—and, the alkali metals or their derivatives are starting materials for the synthesis of so many other metal-organic compounds.

The field of metal-organic compounds is getting increasing attention in the literature, ranging from a pocket-size volume by Coates entitled "Organo-Metallic Compounds," published in England in 1956, to an encyclopedic series on "Synthetic Methods in the Field of Metallo-Organic Compounds," being published in the Soviet Union (a volume on the alkali metals in 1949, mercury in 1945, group III metals in 1945, on antimony, bismuth, niobium, and tantalum in 1947, and the alkali metals in 1949). There has been specific coverage of the organic derivatives of the various metals in this country, as typified by the bibliography on organolithium compounds which has been published at the Lithium Corp. of America. It is hoped that this present symposium will be the first step in a continuing coverage of the over-all field of metal-organic compounds in this country.

This symposium begins with three summary papers surveying the three classes of metal-organic compounds and proceeds to a more detailed consideration of the manufacture, properties, and uses of the metal-organic compounds of 14 of the metals in the 31 papers which comprise the balance of the symposium.

Two contributors came all the way from England to present papers: Dr. Bradley from the University of London, and Dr. Lewis from the Tin Research Institute. There are 19 U. S. industrial organizations represented by the authors, ranging from small manufacturers to the giants of the chemical industry. There is even a paper from the United States Army. It is hoped that the exchange of ideas among the authors and with other participants at this meeting, as well as with the readers of the papers when they are published, will provide many fruitful ideas which will spark the growth of this field.

Leading off the symposium is Henry Gilman of Iowa State College, under whom a number of the authors have done their graduate work, and who comes nearest to being the one individual most closely associated with metal-organic compounds in the world of chemistry today.

Marshall Sittig, *Chairman*

Princeton, N. J.

Organometallic Compounds

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The material presented is an account of studies, largely completed, in several areas. Among them is the report that methylmagnesium iodide is stable for very long periods in diethyl ether. In sharp contrast is the relative instability of some organolithium compounds in tetrahydrofuran. However, techniques have been developed for the preparation and use of RLi compounds in tetrahydrofuran. Among the interesting reactions effected in tetrahydrofuran as a solvent or medium is the cleavage of some heterocycles by lithium; special, synthetically valuable coupling reactions; unusual ratios of carbonation products of 2-quinolyllithium and 1-isoquinolyllithium; and an improved metalation procedure for dibenzofuran which should be applicable to other metalations carried out in tetrahydrofuran systems. *ortho*-Halophenyllithium compounds have been prepared in tetrahydrofuran, and the intermediate benzyne has been established by the Wittig technique using furan.

A general account, partly of a review nature, is presented of the relative reactivities of organometallic compounds, interconversions of organometallic compounds, and the order of activity of some functional groups towards selected organometallic compounds. In addition, there is given a condensation of experimental data on newer studies carried out by coworkers several months before this paper was presented at the symposium in April 1957.

Stability of an Ether Solution of Methylmagnesium Iodide. In connection with studies on the general reactions of organometallic compounds, the stability of Grignard reagents has long been of interest. Previous work (*14*) indicated that the normalities of diethyl ether solutions of various Grignard reagents, as determined by acid titration (*23*), remained essentially unchanged for 4 months. It was necessary to protect the Grignard reagent solutions adequately from the air, but parallel experiments with ethylmagnesium bromide in the light and in the dark indicated that daylight had little effect on the stability of the solutions. Solutions of methylmagnesium iodide are widely used in analytical methods based on the Tschugaeff-Zerewitinoff (*38,42*) analysis for active hydrogen, and as a result their stability has been subjected to some study. A solution of methylmagnesium iodide in di-*n*-amyl ether is reported to be "stable for a month or more" (*36*). When a diisoamyl ether solution of methylmagnesium iodide, prepared for use in an apparatus designed for analysis with Grignard reagents, was analyzed "immediately after its preparation and after it had remained

in its receptacle, exposed to the light for months," the composition of the solution was found to be invariable (*29*).

In connection with the stability of solutions of organometallic compounds in general, it is of interest to compare the above reported stability of methylmagnesium iodide in various solvents with the stability of methyllithium. Methyllithium in diethyl ether and in di-*n*-butyl ether (*5,16*) has been shown to enjoy certain advantages over methylmagnesium halides in the Tschugaeff-Zerewitinoff analysis, partly because of its stability and partly because of the greater solubility of some -OLi compounds over -OMgX compounds. In studies on a modification of the Tschugaeff-Zerewitinoff determination, a di-*n*-butyl ether solution of methyllithium was stored in a Grignard machine (*28*) and the normality of the solution, as determined by gas analysis, was found to have decreased only from 0.777 to 0.764 during 4 months. This indicates that a di-*n*-butyl ether solution of methyllithium is sufficiently stable for use as a valuable supplement to solutions of methylmagnesium iodide in carrying out Tschugaeff-Zerewitinoff analyses.

Further evidence of the stability of methylmagnesium iodide was obtained recently when a sealed Carius tube containing 50 ml. of a diethyl ether solution of about 2*N* methylmagnesium iodide was opened after remaining sealed for 20 years. The normality of the solution was determined by both acid titration and gas analysis and found to be essentially the same as when the solution was first placed in the tube. Of particular significance is the fact that the normality values found by the two different methods of analysis are in close agreement. The normality values obtained by acid titration normally run slightly higher than those obtained by gas analysis, probably because of the presence of basic magnesium compounds formed by means other than hydrolysis of the Grignard reagent, such as ether cleavage and the reaction of the Grignard reagent with traces of water and/or oxygen. Any cleavage of the diethyl ether by the methylmagnesium iodide which might have occurred during the 20 years of storage would have been evidenced by an abnormal difference between the normality values found by acid titration and those found by gas analysis. The average difference was found to be 2.6%, well below the reported average difference of 3.9%.

Positive identification of the material as a solution of methylmagnesium iodide was made by preparing acet-α-naphthalide (*7*) and methylmercuric iodide (*30*) and checking their properties against those of their respective authentic specimens.

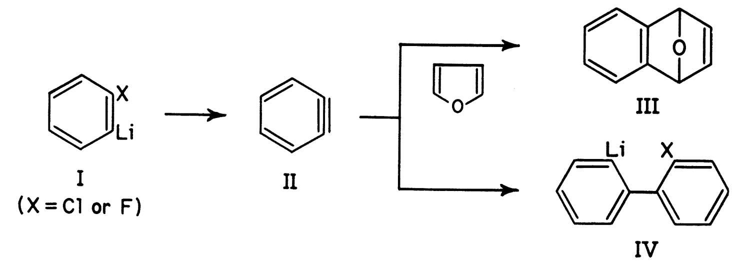
A color test I (*19*), taken immediately after opening the sealed tube, was strongly positive.

It would not be unreasonable to expect variations with other Grignard reagents and variations with other solvents—for example, it is known that methylmetallic compounds may differ appreciably from others (*5,10,16,17*).

Some Reactions of *o*-Halophenyllithium Compounds. As a continuation of earlier studies concerned with *o*-halophenyllithium compounds (*9*), some of their reactions and possible routes by which these organometallic compounds couple to form new organolithium compounds have been investigated further. To obtain a better understanding of the various transformations, the elegant procedure of Wittig and Pohmer (*41*) was employed. These workers successfully interacted *o*-bromofluorobenzene with lithium amalgam in furan to obtain 1,4-dihydronaphthalene-1,4-endoxide (III), a strained molecule which has been formulated as arising via a Diels-Alder reaction between furan and the benzyne intermediate (II). Furthermore, the reactive species (II) has been postulated as being formed from *o*-fluorophenyllithium after the latter has been generated by the interaction of *o*-bromofluorobenzene and lithium amalgam. The same reaction in the absence of furan gives diphenylene and triphenylene (*40*). In view of these results it was hoped that furan could be used in a similar fashion to trap any intermediate which might arise during the break-down of *o*-halophenyllithium compounds (I). *o*-Fluoro- and *o*-chlorophenyllithium were prepared at −60° and −90°, respectively. A relatively large excess of furan was added in each case and then the mixtures were allowed to warm to −50° for the chloro isomer and

—10° for the fluoro isomer. As color test I was positive in both cases at these temperatures, the mixtures were carbonated. The run involving *o*-bromochlorobenzene afforded 41% of III and 11% of 2-carboxy-2′-chlorobiphenyl; with *o*-bromofluorobenzene the yield of III was 67%, while 4% of 2-carboxy-2′-fluorobiphenyl was isolated.

A modified procedure was used with *o*-dibromobenzene, because it was found in previous studies that *o*-bromophenyllithium is a short-lived intermediate. Consequently, *o*-dibromobenzene was added to a mixture of furan and butyllithium. The yield of III was 68%; however, as might be expected, no acid was isolated.

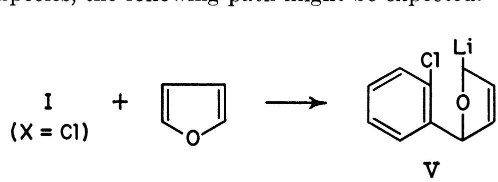


From the foregoing results it is clear that in the case of *o*-chloro- and *o*-fluorophenyllithium some reactive intermediate is competitively reacting with furan and with I. Furthermore, evidence substantiates that such a competitive reaction occurs only when the organolithium compound is formed first independently of the other reactants. In order to ascertain that no metalation reaction ensued between furan and I followed by another similar metalation between the halobenzene and 2-furyllithium at a warmer temperature, an attempt was made to metalate chlorobenzene under conditions used for the competitive reactions. No IV was detected after carbonation; most of the chlorobenzene was recovered.

At this time the most plausible explanation for the presence of coupling product in the competitive reaction is one involving II, although an alternative explanation has been proposed recently for a related reaction (*31*). Intuitively the halide in I would not be expected to be displaced by a nucleophile because the high electron density in the position adjacent to the chlorine atom should hinder such an approach. Also, nucleophilic aromatic substitution reactions are facilitated by electron-withdrawing groups and not electron-donating substituents (*3*). It is conceivable that the anion of I may displace the halogen in another molecule of I either just before or during the formation of the reactive intermediate II. It has been shown that benzyne can be formed via either a stepwise or concerted mechanism, depending on the halogen being eliminated when metalation reactions are involved. However, in this case these findings do not necessarily apply, because it cannot be assumed that the initial step is similar in both cases (*34*).

The rapid conversion of *o*-bromophenyllithium to II did not allow its preparation prior to the addition of furan, and, as a result, the concentration of *o*-bromophenyllithium probably was so slight that the main reaction was between II and furan.

The reaction path leading to III might involve a nucleophilic attack of I on furan or the more probable reaction of II with furan. Of the two possibilities, it appears better to rationalize on the basis that II is the key intermediate. If I is considered as being the attacking species, the following path might be expected.



Evidence indicates that an intermediate such as V is less likely to undergo ring closure to give the highly strained molecule III than would an intermediate arising from interaction of II with furan. If V were formed as an intermediate, ring closure at such a low temperature would be doubtful in view of polar effects and formation of the strained molecule III. Previous studies showed that an intermediate such as 2-(*o*-chlorophenyl)-2′-lithiobiphenyl does not undergo ring closure below approximately −50° to give the planar, nonstrained system, triphenylene.

The formation of V via I is unprecedented, as there is no known instance wherein furan is attacked in such a manner. In fact, under these conditions furan is inert to such an attack and at warmer temperatures the only product formed is 2-furyllithium. In general, metalation reactions proceed smoothly only at room temperature or higher when diethyl ether is the solvent (*18*).

In distinguishing between the two paths it is not pertinent whether the interaction of benzyne with furan is a polar reaction or a four-center type of reaction. As there is no sharp line between the latter two types of reaction mechanisms, it is difficult to rationalize by which one the benzyne interacts with furan (*26*).

On the basis of the afore-mentioned discussion wherein II has been visualized as the intermediate in the various reactions, it would be expected that if I were generated at a temperature above that at which it is stable, the concentration of I would be negligible and no coupling product (IV) should be detected. This has been verified by adding butyllithium to a mixture of furan and an *o*-bromohalobenzene at temperatures considerably higher than those at which the stability of I has been well established. For example, when butyllithium is added to a mixture of *o*-bromochlorobenzene and a large excess of furan, only III has been isolated. No acids were found to be present. The same was true for the fluoro and bromo isomers, although in the latter case the results are not as significant as for the former two.

Organolithium compounds other than butyllithium have been found equally suitable if not somewhat superior for generating the reactive species II at moderate temperatures. A 75% yield of III has been obtained with phenyllithium, while with methyllithium yields up to 84% of III have been isolated. This is surprising because, in the past, methyllithium has been found very ineffective in halogen-metal interconversion reactions. Methyllithium interconverts only with very reactive halides such as *o*-bromoanisole. Phenyllithium is generally more effective but has the disadvantage of occasionally participating in side reactions (*27*). The unusual effectiveness in this case may be attributed to the formation of the highly reactive intermediate, II.

In order to substantiate that a halogen-metal interconversion reaction was the initial step in the reaction between *o*-bromochlorobenzene and phenyllithium, the latter compound was synthesized from iodobenzene and lithium. Recovery of bromobenzene in a good yield supports the above proposal. No attempt was made to recover methyl bromide when methyllithium was used.

No reaction occurred between *o*-dichlorobenzene and butyllithium in the presence of furan. Carbonation, after stirring at room temperature for 1 hour, afforded only 2-furoic acid. It is conceivable that conditions might be varied so as to effect a reaction, as there is evidence that a reaction occurs between butyllithium and *o*-dichlorobenzene in the absence of furan.

Recent related work can be correlated with the results just mentioned together with previous findings (*9*). In the related work, 2,2′-diiodobiphenyl has been postulated as an intermediate in the reaction of *o*-diiodobenzene with butyllithium and lithium in nonpolar solvents (*25*). It is unlikely that *o*-iodophenyllithium would be present as such in any appreciable concentration in view of the instability of *o*-bromophenyllithium at −110°, and especially because a refluxing mixture of benzene and petroleum ether (boiling point, 40° to 60°) was employed. Since the *o*-diiodobenzene was added to butyllithium, an intermediate such as 2-iodo-2′-lithiobiphenyl would be expected to react further with butyllithium to give 2,2′-dilithiobiphenyl. The latter, in turn, could interact with two equivalents of II to give 2,2′-bis-(*o*-lithiophenyl)-bi-

phenyl. This compound could partially couple with butyl iodide, formed during the interconversion reaction, to give 2,2′-bis-(*o*-*n*-butylphenyl)-biphenyl. Alkyl iodides are more prone to be involved in coupling reactions than are other halides. For example, methyl iodide couples with 1-naphthyllithium to give a good yield of 1-methylnaphthalene (*15*). The remaining organodilithium compound would give the corresponding acid after carbonation.

When lithium interacted with *o*-diiodobenzene the major product was triphenylene. This is not too surprising, as it is possible that in this case the intermediate, 2-iodo-2′-lithiobiphenyl, would tend to react preferentially with II instead of with lithium and as a result one would get 2-(*o*-iodophenyl)-2′-lithiobiphenyl, a type of molecule which has been shown to undergo readily ring closure to yield triphenylene.

2-Chloro-2′-(triphenylsilyl)-biphenyl has been prepared by allowing an ethereal solution of *o*-chlorophenyllithium to warm in the presence of triphenylchlorosilane. A small amount of triphenylene was isolated also. The former compound is probably formed via the organolithium compound (IV, $X = \mathrm{Cl}$). The corresponding bromo isomer has been prepared in a less ambiguous manner by means of a mono-halogen-metal interconversion reaction between 2,2′-dibromobiphenyl and butyllithium, followed by reaction with triphenylchlorosilane.

Improved Metalation Procedure for Dibenzofuran. Dibenzofuran has been metalated successfully with various organolithium compounds (*18*). A comparative metalation study of dibenzofuran with *n*-butyllithium has been carried out in diethyl ether, di-*n*-butyl ether, and petroleum ether (boiling point 28° to 38°) to give yields of 56, 76, and 1%, respectively, of 4-dibenzofurancarboxylic acid after carbonation of the metalated product. In all these cases the reaction mixtures were refluxed for 4 to 24 hours; the yields of 4-dibenzofuryllithium increased slightly with increased refluxing periods (*5,16*). The use of organolithium compounds other than *n*-butyllithium generally results in smaller yields of 4-dibenzofuryllithium (*5,16,21*). 4-Dibenzofuryllithium has been derivatized in rather good yields with *o*-methylhydroxylamine and oxygen to give the amine and hydroxy compound, respectively (*12,24*). Although the yields of the latter two compounds were higher than that of the corresponding carboxylic acid, the conditions for preparing the 4-dibenzofuryllithium were similar.

By using tetrahydrofuran as the solvent, dibenzofuran has been metalated with *n*-butyllithium in yields (83 to 86%) higher and under conditions much milder than described previously. The *n*-butyllithium, prepared in diethyl ether, was added to a tetrahydrofuran solution of dibenzofuran at −60° and then the reaction mixture was stirred between 0° and 5° for 1 hour before carbonating. Tetrahydrofuran was purposely selected because it is a more basic solvent than any utilized in previous studies. The base strength of tetrahydrofuran toward boron trifluoride is greater than that of diethyl ether (*2*).

To examine further the pronounced effect of tetrahydrofuran on the metalation of dibenzofuran, a run was made at −50°. A significant 11% yield of acid was obtained after stirring at −50° for 1 hour followed by carbonation. In contrast, a diethyl ether solution of dibenzofuran and butyllithium stirred at 0° for 1 hour afforded only a 5% yield of acid.

It was hoped that exclusion of diethyl ether from the reaction might result in metalation under even milder conditions than mentioned. For this purpose the *n*-butyllithium was prepared *in situ* at −25° from butyl chloride, to avoid loss of the RLi compound. It has been observed that the yield of butyllithium decreases more rapidly in tetrahydrofuran than in diethyl ether. The highest yield of acid obtained with this method was 30%. The use of butyl bromide instead of butyl chloride did not give higher yields.

Lithium Cleavages of Some Heterocycles in Tetrahydrofuran. Cleavages of heterocycles using various media and cleaving agents has often proved to be a valuable tool in synthesis and structure proof.

Refluxing lithium and dibenzofuran in diethyl ether for 22 hours afforded excellent yields of 3,4-benzocoumarin when the reaction was terminated by carbonation. When refluxing dioxane was used as the solvent, only 2-hydroxybiphenyl was obtained upon hydrolysis or carbonation after 12 hours (*6*).

Dibenzo-*p*-dioxin has been cleaved by lithium in refluxing diethyl ether (24 hours) to yield upon carbonation 23% of 2-hydroxy-2′-carboxydiphenyl ether. This molecule could presumably be cleaved in refluxing dioxane.

In refluxing diethyl ether, lithium does not cleave dibenzothiophene even after 36 hours. However, dibenzothiophene can be cleaved by lithium in refluxing dioxane over a period of 12 hours to yield biphenyl and 2-mercaptobiphenyl after hydrolysis or carbonation (*6*). This again demonstrates the destructive nature of refluxing dioxane on organometallic compounds.

Attempts to cleave *N*-ethylcarbazole with lithium in refluxing dioxane have resulted in essentially quantitative recovery of starting material after 24 hours (*11*). The cleavage was not attempted in ether, but a negative result may be a fairly safe assumption. Carbazole gave the same results under identical conditions.

When purified tetrahydrofuran was used, all the afore-mentioned compounds have undergone cleavage with significant ease. In all cases the reactions were exothermic, giving rise to a dark blue-green color. Color test I was usually positive within 2 minutes after the reactants were mixed. In many instances, the dark blue-green color gradually turned to a dark brown. For comparison purposes, the reactions were all run for 45 minutes and then either hydrolyzed or carbonated.

Dibenzothiophene and dibenzo-*p*-dioxin reacted completely durmg the allotted time. Both reactions approached the reflux temperature of tetrahydrofuran if they were not controlled.

Dibenzo-*p*-dioxin gave the normal products upon carbonation in better yield than the corresponding diethyl ether cleavage, but dibenzothiophene produced 3,4-benzothiocoumarin and the disulfide of 2-mercapto-2′-carboxybiphenyl. These are probably formed from the 2-mercapto-2′-carboxybiphenyl during the work-up. A small amount of biphenyl was also obtained from the uncontrolled reactions of dibenzothiophene. A maximum yield of cleavage products was realized at 25° for dibenzothiophene and dibenzo-*p*-dioxin, using an ice bath to moderate the reactions.

In the case of dibenzofuran, it was best to use a higher temperature, because a 75% recovery of starting material resulted at 25°. The uncontrolled reactions which warmed up to 40° to 50° gave a 20% yield of 3,4-benzocoumarin after carbonation.

Cleavage of thianthrene at 25° with lithium yielded no identifiable products, but 90% of the starting material was in the form of an unpleasant smelling acidic oil after carbonation. This evidence plus the fact that color test I was positive can be reconcilable only with cleavage of this heterocycle. When using refluxing diethyl ether as the solvent, 72% of thianthrene was recovered, even though color test I was positive after 1 hour.

No products have been identified from the lithium cleavage of *N*-ethylcarbazole in tetrahydrofuran. Some cleavage must have occurred, as only 75% of the starting material was recovered after 45 minutes of refluxing and color test I was positive. The infrared spectra of some of the recovered oils showed an N-H band. Lithium in refluxing tetrahydrofuran for 45 minutes failed to cleave carbazole, giving a 90% recovery of starting material.

While dibenzofuran cleaved rather easily in ether, dibenzothiophene resisted cleavage under these conditions. However, in tetrahydrofuran, dibenzothiophene gave the best yield of cleavage product at 25°, whereas dibenzofuran was appreciably cleaved only at higher temperatures.

A noteworthy deviation from heterocycles was the cleavage of diphenyl ether to yield phenol, benzoic acid, and 2-carboxydiphenyl ether after carbonation. The last product may be accounted for by assuming metalation of the diphenyl ether by phenyllithium obtained by cleavage of the diphenyl ether.

Coupling Reactions with Some Organolithium Compounds in Tetrahydrofuran. Depending upon conditions and solvents used, a variety of products have been obtained from reactions of dihalobenzene compounds with *n*-butyllithium. One investigation (*25*) described the reactions of *o*-diiodobenzene and *o*-dibromobenzene with magnesium, lithium, and *n*-butyllithium in various solvents to yield a series of coupling products. The formation of these coupling products in the reactions involving *o*-diiodobenzene has been postulated to proceed through the initial formation of 2,2′-diiodobiphenyl as an intermediate. However, neither 2,2′-diiodobiphenyl nor 2,2′-dibromobiphenyl could be isolated from the reaction mixtures.

Another investigation (*9*) described the reactions of *o*-dibromobenzene, *o*-chlorobromobenzene, and *o*-fluorobromobenzene with *n*-butyllithium in ethereal solution at low temperatures to yield upon carbonation *o*-bromobenzoic, *o*-chlorobenzoic, and *o*-fluorobenzoic acids, respectively. When the reaction mixtures were warmed prior to carbonation, the various *o*-halophenyllithium reagents underwent coupling reactions to yield such products as 2-halo-2′-lithiobiphenyl, 2-(*o*-halophenyl)-2′-lithiobiphenyl, and triphenylene. However, in no case was any 2,2′-dihalobiphenyl isolated.

Additional work has shown that one equivalent of an ethereal solution of *n*-butyllithium reacts instantaneously at −78° with two equivalents of *o*-dibromobenzene, dissolved in tetrahydrofuran, to give, as the main product, 2,2′-dibromobiphenyl in yields ranging from 67 to 74%. Similarly, when *p*-dibromobenzene and *p*-chlorobromobenzene were dissolved in tetrahydrofuran and treated with an ethereal solution of *n*-butyllithium in a 2 to 1 ratio, there resulted 4,4′-dibromobiphenyl and 4,4′-dichlorobiphenyl, respectively. However, the yields of the latter two compounds were much lower than that of 2,2′-dibromobiphenyl.

Although the mechanism of the reaction in tetrahydrofuran has not been extensively studied, it is conceivable that *o*-bromophenyllithium is formed as an intermediate via a halogen-metal interconversion reaction between *o*-dibromobenzene and *n*-butyllithium, and that this in turn can couple with *o*-dibromobenzene to give the final product, 2,2′-dibromobiphenyl.

From the foregoing discussion, there is a strong inference that the solvent may play an important role in the reaction of *n*-butyllithium with a dihalobenzene compound. In further support of this conclusion, it has been found that when *o*-dibromobenzene interacts with *n*-butyllithium in diethyl ether under identical conditions and with the same quantities of reactants employed in the run carried out in tetrahydrofuran, no 2,2′-dibromobiphenyl was isolated. The only products were an unidentified ether-insoluble material and a highly viscous oil.

p-Chlorobromobenzene and *p*-dibromobenzene, when reacted with *n*-butyllithium in diethyl ether, undergo a normal halogen-metal interconversion reaction to give *p*-chlorophenyllithium and *p*-bromophenyllithium, respectively, in high yields (*13*). However, it is apparent that the mode of reaction is changed when tetrahydrofuran is used as the solvent.

This preparation of 2,2′-dibromobiphenyl is interesting also from a synthetic viewpoint, as previous to this, the only satisfactory means for preparing 2,2′-dibromobiphenyl was a multistep process involving diazotization of 2,2′-diaminobiphenyl (*4,35*). The procedure just described offers several advantages over the older methods. The over-all yield is probably higher, there are fewer steps involved, and the reaction can be achieved rapidly.

This reaction is now finding extensive use for the preparation of 2,2′-dibromobiphenyl, which is an important intermediate in the preparation of some cyclic organosilicon compounds (*8*).

Effect of Solvent on Course of Carbonation Reaction of 2-Quinolyl- and 1-Isoquinolyllithium. In a recent splendid investigation, Normant (*32*) found that excellent yields of the Grignard reagents could be obtained with alkenyl and aryl chlorides by employing tetrahydrofuran as the solvent. This solvent has been used further to include the preparation of phenyllithium from chloro- and fluorobenzene (*33*) with

lithium wire, and 2-quinolyllithium from 2-bromoquinoline by means of a halogen-metal interconversion reaction with *n*-butyllithium at −60°.

On carbonating 2-quinolyllithium, which was prepared in tetrahydrofuran, by pouring jetwise onto a slurry of dry ice–tetrahydrofuran, the 2-quinolinecarboxylic acid was obtained in a yield of 50%. The same intermediate, however, when made in diethyl ether and carbonated by employing a dry ice–ether slurry, yields 2,2′-diquinolyl ketone in 20% yield and no acid. When this intermediate in diethyl ether was carbonated at −100°, both acid and ketone were obtained.

Ketone formation on carbonation of organolithium derivatives has been noted (*22*). This reaction has been shown to involve the initial formation of the carboxylic salt which is again attacked by the organolithium reagent (*1*). The intermediate was found to be the dilithio ketal, which resisted further substitution or loss of lithium oxide.

As the stability of the ketal was shown to be enhanced by the presence of electron-attracting groups (*37*), the electrostatic effect of the nitrogen atom can be considered to have been involved in the stabilization of the quinolyl ketal. Further evidence in support of this hypothesis was the isolation of only the acids on carbonation of 3-quinolyl- and 4-isoquinolyllithium under the same conditions.

The greater basicity and solvating effect of tetrahydrofuran may have been responsible for reducing the effective formation of the intermediate ketal which would result in the production of the acids in preference to the ketones.

2-Quinolyl- and 1-isoquinolyllithium have been prepared for the first time. The general procedure used was a low temperature halogen-metal interconversion reaction with *n*-butyllithium. Each of these organolithium compounds was characterized by a reaction with benzophenone to give the corresponding tertiary alcohols. 3-Quinolyllithium was reported earlier (*20*), and 2-quinolylmagnesium bromide has been prepared with difficulty and in low yield (*39*).

Incidental to other interesting effects of tetrahydrofuran as a solvent, mention should be made of the following. First, an R_3SiH compound reacts with RLi, but not with RMgX, in diethyl ether to give R_4Si types; however, the Grignard reagent does undergo a related reaction in tetrahydrofuran. Second, tetrahydrofuran is not only a good solvent for reactions involving sparingly soluble organosilicon and organogermanium compounds, but also improves numerous reactions of these and related types. For example, the cleavage of hexaaryldisilanes and hexaaryldigermanes by lithium to give R_3MLi types is much more effectively carried out in tetrahydrofuran. Also, hexaethyldisilane reacts with lithium in tetrahydrofuran. Third, in the reaction of *o*-dibromobenzene with allylmagnesium chloride in tetrahydrofuran there are formed, subsequent to carbonation, significant quantities of *o*-allylbenzoic acid. Details will be presented on the preparation of RLi compounds for RF, RCl, and RBr compounds in tetrahydrofuran, and their stabilities in this and some other solvents.

Acknowledgment

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Metal Alkoxides

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The metal alkoxides constitute an important class of compounds characterized by the metal-oxygen-carbon bonding system. The strongly electronegative oxygen atom induces considerable polarity in the $\overset{\delta+\delta-}{\text{M-O}}$ bond, but this may be partially offset by the electrophilic nature of metals that undergo covalency expansion by coordination with donor atoms. The properties of the M-O-C system are also affected by the electronic behavior of the alkyl group. Its configuration gives rise to important stereochemical effects. The metal alkoxides offer great scope for producing compounds with varied chemical and physical properties. It is surprising that only the alkoxides of magnesium and aluminum were of industrial importance until a few years ago.

The methods of preparing the alkoxides are varied and reflect in an interesting way the chemistry of the metals. The simplest method, involving the reaction of the metal with an alcohol (Equation 1), appears to be confined to the alkali metals, magnesium and aluminum.

$$M + nROH \rightarrow M(OR)_n + n/2H_2 \quad (1)$$

Even in this reaction the effect of the alkyl group is apparent, as *tert*-butyl alcohol reacts much less rapidly with sodium than does methyl or ethyl alcohol. Moreover, the reactivity of an alkali metal depends on its electropositivity and thus potassium combines more rapidly with the tertiary alcohol than sodium. In contrast to the alkali metals magnesium and aluminum require catalysts—e.g., iodine and mercuric chloride, respectively—to initiate the reaction between metal and alcohol. The behavior of thallium merits special mention. Lamy (*110*) found that thallium did not react when suspended in boiling ethyl alcohol, yet a piece of the metal held in air over the surface of the alcohol readily combined to form thallous ethoxide. Apparently the metal is oxidized in air and the oxide undergoes a reversible reaction with alcohol:

$$4Tl + O_2 \rightarrow 2Tl_2O \quad (2)$$

$$Tl_2O + 2EtOH \rightarrow TlOEt + TlOH \quad (3)$$

$$TlOH + EtOH \rightleftharpoons TlOEt + H_2O \quad (4)$$

According to Menzies (*130*) the very low solubility of thallous ethoxide in ethyl alcohol favors its formation in Equation 4.

As an alternative to the direct reaction, Equation 1, the alkoxide may be obtained by combination of a metal oxide (or hydroxide) with alcohol as illustrated in Equations

3 and 4. Thus sodium ethoxide may be produced from sodium hydroxide and ethyl alcohol by azeotropic dehydration using benzene. The removal of water disturbs the equilibrium in Equation 4 and conversion to the ethoxide becomes complete. The reversibility of the sodium hydroxide–ethyl alcohol reaction also imposes limitations on the efficiency of sodium as a reagent for drying aqueous ethyl alcohol. Vanadyl alkoxides, $VO(OR)_3$ (*142*), have been obtained by the prolonged treatment of hydrated vanadium pentoxide with alcohols.

A third method of preparation of the alkoxides depends on the metal chloride as starting material. This method has been widely applied in the preparation of alkoxides which cannot be obtained by the first method. In the chloride method the detailed procedure depends on the reactivity of the chloride and also on the properties of the metal alkoxide. For example, among the elements in Group IV of the periodic classification, silicon alone forms a chloride sufficiently reactive towards alcohols to undergo complete replacement of chlorine by alkoxide groups.

$$SiCl_4 + 4ROH \rightarrow Si(OR)_4 + 4HCl \quad (5)$$

This reaction was discovered by Ebelman (*74*) in 1846. With the tetrachlorides of titanium (*102*), zirconium (*34*), and thorium (*45*), the degree of substitution decreases with increase in atomic number of the central atom:

$$TiCl_4 + 3ROH \rightarrow TiCl_2(OR)_2,ROH + 2HCl$$

$$2ZrCl_4 + 5ROH \rightarrow ZrCl_3(OR),ROH + ZrCl_2(OR)_2,ROH + 3HCl$$

$$ThCl_4 + 4ROH \rightarrow ThCl_4,4ROH$$

Similarly, the pentachlorides of niobium and tantalum (*77*) undergo trisubstitution:

$$Nb(Ta)Cl_5 + 3ROH \rightarrow Nb(Ta)Cl_2(OR)_3 + 3HCl$$

The author and others have recently found that vanadium tetrachloride resembles titanium tetrachloride in its reactions with alcohols, while molybdenum pentachloride differs from niobium and tantalum pentachlorides by undergoing disubstitution (*43*):

$$MoCl_5 + 2ROH \rightarrow MoCl_3(OR)_2 + 2HCl$$

An interesting feature of these reactions involving metal chlorides and alcohols is that although the replacement of chlorine is not complete, yet the partial replacement occurs very rapidly and exothermically. Furthermore, prolonged treatment of the resultant metal chloride alkoxide with excess boiling alcohol fails to cause further reaction. This behavior was emphasized by the discovery that metal chloride alkoxides undergo alcohol interchange (*32, 138*).

$$ZrCl_2(OEt)_2,EtOH + 3Pr^iOH \rightarrow ZrCl_2(OPr^i)_2,Pr^iOH + 3EtOH$$

$$ZrCl(OPr^i)_3,Pr^iOH + 3CH_3OH \rightarrow ZrCl(OCH_3)_3 + 4Pr^iOH$$

In order to prepare the metal alkoxide it is necessary to employ a base which will cause further replacement of chlorine. In fact, attempts were made as early as 1875 (*69*) to prepare titanium tetraethoxide by the reaction involving titanium tetrachloride, ethyl alcohol, and sodium ethoxide. However, it remained for Bischoff and Adkins (*11*) in 1924 to demonstrate the effectiveness of this method:

$$TiCl_4 + 3ROH \rightarrow TiCl_2(OR)_2,ROH + 2HCl$$

$$TiCl_2(OR)_2,ROH + 2NaOR \rightarrow Ti(OR)_4 + 2NaCl + ROH$$

Nevertheless, Meerwein and Bersin (*122*) found that zirconium alkoxides could not be obtained by a similar method, because of the formation of stable double alkoxides. They claimed that the acid sodium zirconium ethoxide, $NaH[Zr(OEt)_6]$, was produced in accordance with the requirements of the following equation:

$$ZrCl_4 + 5NaOEt + EtOH \rightarrow NaH[Zr(OEt)_6] + 4NaCl \quad (6)$$

The zirconium tetraethoxide was then obtained by treatment of the acid sodium zirconium ethoxide with the equivalent amount of alcoholic hydrogen chloride.

$$NaH[Zr(OEt)_6] + HCl \rightarrow Zr(OEt)_4 + NaCl + 2EtOH$$

Their formulation of the acid sodium zirconium ethoxide was supported by titration of zirconium tetraethoxide dissolved in benzene with 2*N* sodium methoxide. Using thymolphthalein indicator, they obtained an end point corresponding to the reaction of one equivalent of sodium methoxide per atom of zirconium. Repeated experiments in these laboratories have failed to confirm the detailed reactions claimed by Meerwein and Bersin, although the author agrees that a double complex formed in the reaction prevents the isolation of zirconium tetraethoxide (*48*). However, it has been found that by using anhydrous ammonia in place of sodium ethoxide the tetraalkoxides of zirconium could be obtained directly (*47, 48*):

$$ZrCl_4 + 4ROH + 4NH_3 \rightarrow Zr(OR)_4 + 4NH_4Cl \qquad (7)$$

Nelles (*133*) had previously shown that titanium alkoxides could be obtained from the reaction involving titanium tetrachloride, alcohol, and ammonia, and this method has since been confirmed by several workers and is used on an industrial scale (*16, 64, 65, 109, 136, 140, 141*). Recently, Herman (*92, 93, 164*) has introduced an interesting modification of the ammonia method. The reaction of titanium tetrachloride, alcohol, and ammonia is carried out in the presence of an amide—e.g., formamide—or nitrile, so that the titanium alkoxide forms an upper layer while the ammonium chloride remains in solution in the lower layer and no filtration is required.

Recent work (*28, 49–51*) has shown that the ammonia method is satisfactory for the preparation of the pentaalkoxides of niobium or tantalum from their pentachlorides:

$$MCl_5 + 5ROH + 5NH_3 \rightarrow M(OR)_5 + 5NH_4Cl \qquad (8)$$

On the other hand, the ammonia method failed to produce a chloride-free product in attempts to prepare thorium tetraalkoxides from the tetrachloride. Fortunately, the sodium method was effective (*44, 46*), presumably because thorium does not form stable double alkoxides with sodium (cf. zirconium).

$$ThCl_4{,}4ROH + 4NaOR \rightarrow Th(OR)_4 + 4NaCl + 4ROH \qquad (9)$$

Moreover, it was found that the thorium alkoxides were stronger bases than ammonia in alcoholic solution and this probably explains the failure of the ammonia method to yield a pure thorium tetraalkoxide,

$$Th(OR)_4 + NH_4^+ \rightarrow Th(OR)_3^+ + NH_3 + ROH \qquad (10)$$

$$Th(OR)_3^+ + Cl \rightleftharpoons ThCl(OR)_3 \qquad (11)$$

The success of the sodium method would thus be due to the stronger basicity of the alkoxide ion relative to the thorium alkoxide coupled with the smaller solubility of sodium chloride compared with ammonium chloride.

It can now be seen how the method of preparation of a metal alkoxide from the metal chloride is largely dictated by the properties of the metal alkoxide. The alkyl group may play an equally important part. For example, the reactions involving alcohols containing an electron-releasing alkyl group—e.g., tertiary alcohols—lead to the formation of hydrolyzed metal alkoxides. Although the details of the hydrolytic mechanism have not yet been completely elucidated, methods of suppressing this alternative reaction have been found. Thus Cullinane and others (*64, 65*) showed that the presence of a base (pyridine) with the tertiary alcohol was an essential factor in the preparation of titanium tetra-*tert*-butoxide from the tetrachloride. This method of preparation has been confirmed and it has also been shown that dipyridinium hexachlorozirconate, $(C_5H_6N)_2ZrCl_6$, is a better starting material than the tetrachloride for preparing zirconium alkoxides. These facts are consistent with the view (*33*) that

the hydrolysis is a consequence of a secondary reaction (Equation 13) involving the hydrogen chloride (from the primary reaction 12) and the tertiary alcohol:

$$MCl_n + ROH \rightarrow MCl_{n-1}(OR) + HCl \quad (12)$$

$$HCl + ROH \rightarrow RCl + H_2O \quad (13)$$

In Cullinane's method the pyridine combines with the hydrogen chloride (Equation 12) and thus prevents reaction (Equation 13). Similarly no hydrolysis occurs when $(C_5H_6N)_2ZrCl_6$ is used, because this compound does not react with alcohols and no hydrogen chloride is produced. Haslam (*88*) has developed an alternative to Cullinane's method by first forming the metal chloride ammoniate ($TiCl_4 \cdot 8NH_3$) and causing this to react with an alcohol in an inert solvent.

In the case of quadrivalent cerium it was necessary to use the complex chloride, $(C_5H_6N)_2CeCl_6$, because the tetrachloride does not exist. However, a representative number of stable cerium(IV) alkoxides have been prepared including some volatile monomeric liquids (*29, 30*).

$$(C_5H_6N)_2CeCl_6 + 4ROH + 6NH_3 \rightarrow Ce(OR)_4 + 6NH_4Cl + 2C_5H_5N$$

Gilman and others (*83*) have recently introduced an ingenious method for preparing insoluble alkoxides. They prepared uranium tetramethoxide by allowing lithium methoxide to react with uranium tetrachloride in methanol. The insoluble uranium tetramethoxide was isolated by filtration from the methanolic solution of lithium chloride

$$UCl_4 + 4LiOMe \rightarrow U(OMe)_4 + 4LiCl$$

The same authors prepared uranium(IV) alkoxides by an alternative method involving alcoholysis of the uranium tetradiethylamide:

$$4LiNEt_2 + UCl_4 \rightarrow U(NEt_2)_4 + 4LiCl$$

$$U(NEt_2)_4 + 4ROH \rightarrow U(OR)_4 + 4Et_2NH$$

Novel methods were also employed by Gilman and others (*81, 82*) in preparing uranium(V) pentaalkoxides. In one example the pentaalkoxide was obtained by air oxidation of the uranium(IV) tetraalkoxide, apparently according to the requirements of the following equation:

$$5U(OEt)_4 + O_2 \rightarrow 4U(OEt)_5 + UO_2 \quad (14)$$

An alternative method involved oxidation with bromine followed by treatment with sodium ethoxide:

$$2U(OEt)_4 + Br_2 \rightarrow 2UBr(OEt)_4$$

$$UBr(OEt)_4 + NaOEt \rightarrow U(OEt)_5 + NaBr$$

Another unusual method for the preparation of alkoxides is due to Boyd (*17*), who has prepared titanium alkoxides by causing alcohols to react with titanium disulfide. Titanium alkylamides may be prepared by an analogous method (*17*).

Finally, mention must be made of the method of alcohol interchange (alcoholysis):

$$M(OR)_n + nR'OH \rightleftharpoons M(OR')_n + nROH \quad (15)$$

It appears that the metal alkoxides undergo spontaneous alcohol interchange in solution in striking contrast to tetraalkyl orthosilicates, which (when pure) require the presence of either acidic or basic catalysts. By suitable choice of group R in Equation 15 the new alkoxide, $M(OR')_n$, may be obtained quantitatively. It is usual to start with a lower alkoxide, $M(OR)_n$, so that the lower alcohol, ROH, is easily separated from R'OH by distillation. The method is particularly useful where the alcohol R'OH is reactive—e.g., unsaturated alcohols or higher tertiary alcohols. Moreover, by conducting the reaction in an inert solvent, quantitative yields may be obtained using the

theoretical quantities of reactants. The system described by Equation 15 is reversible and it is possible to produce a lower alkoxide from a higher alkoxide by employing a large excess of the lower alcohol. In some cases—e.g., methoxides—the lower alkoxides are insoluble and the interchange is thus facilitated.

Mehrotra (*125*) has shown that alkoxides can be obtained by an analogous trans-esterification process.

$$M(OR)_4 + 4R''CO_2R' \rightarrow M(OR')_4 + 4R''CO_2R \quad (16)$$

This method was particularly useful for the preparation of zirconium or hafnium tertiary butoxides which cannot be readily obtained by any of the foregoing methods.

This account of preparative methods would not be complete without some mention of mixed alkoxides $M(OR)_x(OR')_{n-x}$. In general these compounds appear to be unstable, because of disproportionation into the single alkoxides, but in certain cases stable mixed alkoxides have been obtained. Thus in attempting to prepare zirconium tetra-*tert*-butoxide from either the methoxide or ethoxide by alcohol interchange it was found that the reactions ceased with the formation of mixed alkoxides (*40*). Mehrotra (*129*) investigated these systems further and isolated the mixed alkoxides according to the following reactions:

$$Zr(OMe)_4 + 3Bu^tOH \rightarrow Zr(OMe)(OBu^t)_3 + 3MeOH$$

$$Zr(OBu^t)_4 + ROH \rightarrow Zr(OR)(OBu^t)_3 + Bu^tOH$$

$$Zr(OBu^t)_4 + 2ROH \rightarrow Zr(OR)_2(OBu^t)_2 + 2Bu^tOH$$

The same author has also prepared some mixed alkoxides of aluminum by similar methods (*126, 128*). Mixed alkoxides of titanium were obtained by Nesmeyanov and Nogina (*139*), who utilized the titanium chloride–alkoxides:

$$TiCl(OR)_3 + R'OH + NH_3 \rightarrow Ti(OR')(OR)_3 + NH_4Cl$$

Titanium mixed alkoxides containing three different alkoxide groups were prepared by Ghosh *et al.* (*79, 80*) by the following sequence of reactions:

$$TiCl_2(OR)_2 + R'OH + C_5H_5N \rightarrow TiCl(OR')(OR)_2 + C_5H_5N{,}HCl$$

$$TiCl(OR')(OR)_2 + R''ONa \rightarrow Ti(OR'')(OR')(OR)_2 + NaCl$$

Chemical Properties

The dominating property of the metal alkoxides is the characteristic facility to hydrolyze through to the metal oxide. In fact, metal alkoxides will react with practically any compound which contains hydroxyl groups. Thus, a ready alcohol interchange or an interchange involving a phenol is found. Furthermore, compounds which can be transformed to hydroxy derivatives by enolization will also be reactive, and zirconium alkoxides combine vigorously and exothermically with β-diketones to form the tetrakischelate derivatives in which the metal exhibits the coordination number 8. In contrast, titanium alkoxides undergo disubstitution to form the bischelate dialkoxide in which titanium exhibits its maximum covalency of 6. It might be argued that the β-diketones constitute a special case because of the stabilization conferred by chelation; however, Haslam (*91*) has recently claimed the formation of alkenyl oxides of titanium by treating the titanium alkoxide with aldehydes:

$$Ti(OPr^i)_4 + 2CH_3CHO \rightarrow Ti(OCH{=}CH_2)_2(OPr^i)_2 + 2Pr^iOH$$

It seems reasonable to suppose that this reaction proceeds by alcohol interchange involving the vinyl alcohol formed by enolization of the aldehyde.

The author was particularly interested to find that titanium or zirconium alkoxides would not combine with mercaptans to form metal mercaptides although the thiol hydrogen atom is more acidic than the alcoholic hydroxyl hydrogen atom. Thus it appears that the electron donor power of the atom adjacent to the active hydrogen

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atom is important in these exchange reactions which may well be initiated by a coordination mechanism:

$$R'OH + M(OR)_n \rightarrow \left[\begin{array}{c} R'\text{—}O \rightarrow M(OR)_{n-1} \\ H\cdots O \\ \quad R \end{array}\right] \rightarrow R'OM(OR)_{n-1} + ROH$$

The failure of mercaptans to interchange with metal alkoxides would then be ascribed to ineffective coordination between sulfur and the metal.

Exchange reactions readily occur between the halogen acids and metal alkoxides, and Mehrotra (*127*) has shown that the products of the reactions involving hydrogen chloride and the alkoxides of silicon, titanium, and zirconium are the same as the products of the reactions of the tetrachlorides with alcohols.

Metal alkoxides also combine with acetyl chloride and in several cases the chloride alkoxide formed in the reaction adds on a molecule of alkyl acetate (*31*, *37*, *102*):

$$Ti(OEt)_4 + 4CH_3COCl \rightarrow TiCl_4,CH_3CO_2Et + 3CH_3CO_2Et$$

$$Ti(OEt)_4 + 3CH_3COCl \rightarrow TiCl_3(OEt),CH_3CO_2Et + 2CH_3CO_2Et$$

$$Zr(OEt)_4 + 4CH_3COCl \rightarrow ZrCl_4,CH_3CO_2Et + 3CH_3CO_2Et$$

$$Zr(OPr^i)_4 + 4CH_3COCl \rightarrow ZrCl_4,2CH_3CO_2Pr^i + 2CH_3CO_2Pr^i$$

$$Zr(OPr^i)_4,Pr^iOH + 2CH_3COCl \rightarrow ZrCl_2(OPr^i)_2,Pr^iOH + 2CH_3CO_2Pr^i$$

Zirconium tetrachloride combines with either one molecule of ethyl acetate or two molecules of isopropyl acetate, while the dichloride diisopropoxide of zirconium prefers to coordinate with isopropyl alcohol rather than with isopropyl acetate. The mechanisms of these reactions have not yet been elucidated but it is significant that reactions involving tertiary alkoxides of titanium or zirconium with acetyl chloride show certain peculiarities (*31*, *37*). For example, with zirconium *tert*-amyl oxide and acetyl chloride the first substitution (Equation 17) is rapid, but further substitution takes place very slowly even in the presence of an excess of acetyl chloride.

$$Zr(OCMe_2Et)_4 + CH_3COCl \rightarrow ZrCl(OCMe_2Et)_3 + CH_3CO_2CMe_2Et \qquad (17)$$

In the case of titanium *tert*-amyl oxide the effect is still more marked (*37*) and it is clear that stereochemical effects are operative in these reactions.

Another characteristic property of metal alkoxides is evident in the facile reactions between the alkoxides and the tetrachlorides or chloride alkoxides. Thus quantitative yields of the hitherto inaccessible titanium trichloride monoalkoxides (*37*) were obtained by causing the tetraalkoxide to react with the tetrachloride (in excess):

$$3TiCl_4 + Ti(OR)_4 \rightarrow 4TiCl_3(OR)$$

[see also (*134*)].

Zirconium alkoxides behaved similarly (*31*):

$$ZrCl_2(OPr^i)_2,Pr^iOH + Zr(OPr^i)_4,Pr^iOH \rightarrow 2ZrCl(OPr^i)_3,Pr^iOH$$

Although reactions involving silicon esters and silicon tetrachloride occur slowly at elevated temperatures (*78*), yet silicon esters and titanium tetrachloride undergo vigorous reactions (*94*). These reactions are now being studied in the author's laboratories.

Nesmeyanov and others (*137*) have investigated the action of halogens on titanium alkoxides. When either chlorine or bromine was used, the product was the titanium dihalide dialkoxide alcoholate $TiX_2(OR)_2,ROH$.

Metal alkoxides have long been of importance in organic chemistry because of their behavior with carbonyl compounds. Thus the basic alkoxides promote enolization and condensation—e.g., aldolization of aldehydes (*91*). In 1906 Tischchenko discovered that aluminum alkoxides cause the conversion of aldehydes into esters (*163*).

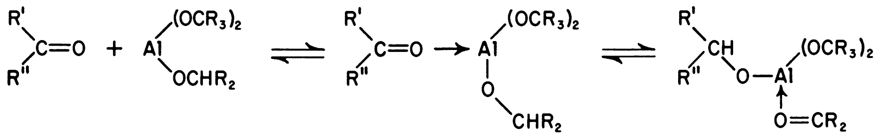
$$2RCHO \rightarrow RCO_2CH_2R$$

Recent work by Villani and Nord (*168*) has revealed how the condensation of aldehydes is affected by the acidic or basic nature of the metal alkoxide catalyst. Aluminum ethoxide, which behaves as a "Lewis acid" because of the electrophilic nature of the aluminum, produces simple esters by the Tischchenko reaction. On the other hand, the mildly basic double alkoxides such as $Mg[Al(OEt)_4]_2$, $Ca[Al(OEt)_4]_2$, $Na_2[Mg(OEt)_4]$, $Mg(OEt)_2$, or $Ca(OEt)_2$, cause the formation of trimeric glycol esters:

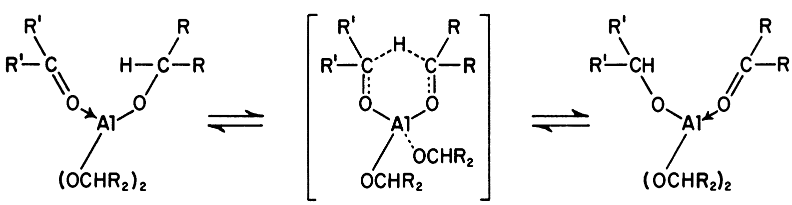
$$3RCH_2\cdot CHO \rightarrow RCH_2\underset{\displaystyle OH}{\underset{|}{C}H}\cdot CHR\cdot CH_2O_2C\cdot R$$

The strongly basic sodium ethoxide caused only the aldol-type condensation. Lin and Day (*112*) have studied the "mixed" Tischchenko reaction in which propionaldehyde was allowed to condense with other aldehydes in the presence of a catalytic quantity of aluminum isopropoxide in carbon tetrachloride solution. They found that the mixed esters produced in highest yield were those derived from the acid of the aldehyde which undergoes the simple Tischchenko reaction more readily.

Another important reaction involving metal alkoxides and carbonyl compounds is the Meerwein-Ponndorf-Verley-Oppenauer oxidation-reduction system. Although alkoxides of sodium or magnesium were originally used to catalyze the reaction, it was later shown by Meerwein and others (*124*) that alkoxides of aluminum, zirconium, tin(IV), titanium, antimony, or iron were also effective. The readily available aluminum alkoxides are most used because they are generally less inclined to cause the alternative condensation reactions. Meerwein (*121*) suggested that the reaction mechanism involves the preliminary coordination of the carbonyl oxygen to the electrophilic aluminum to form an intermediate complex compound:



In view of recent work (*100, 117, 145, 171, 175*), there seems little doubt that the reaction proceeds via an intramolecular transfer of an incipient hydride ion from carbinol to carbonyl carbon atoms and that a cyclic transition state is involved:



Thus experiments using tracer deuterium either on solvent molecules (*71, 145*) or on the carbinol carbon atom (*171*) gave results in agreement with this mechanism. The cyclic transition state is susceptible to stereochemical influences and this has been confirmed by Jackman and others (*99, 101*) and by Doering and Young (*72*). The results obtained by Doering and Aschner (*71*) show that a free radical mechanism is extremely unlikely.

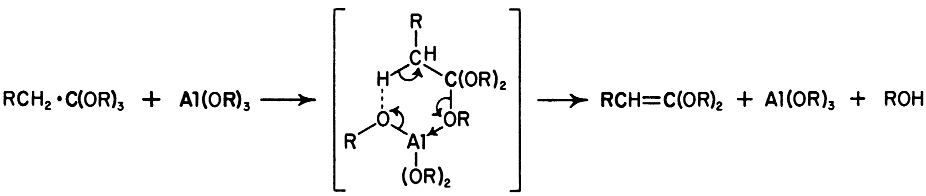
As a consequence of the mechanism depicted in Equation 18 it is clear that the partial positive charge induced on the carbonyl carbon atom facilitates the hydrogen

transfer and hence affects the rate of reaction and the position of equilibrium. This electronic aspect of the mechanism was quantitatively confirmed by McGowan in 1951 using data concerning the substituted acetophenones $X \cdot C_6H_4 \cdot CO \cdot CH_3$ (*117*). Jackman and Macbeth (*98*) have studied the kinetics of reductions with aluminum alkoxides. They used an elegant technique involving the racemization of the aluminum derivative of an optically active alcohol by the corresponding ketone, thus avoiding the complications of employing two ketones and forming mixed alkoxides. The reaction rate conformed to the following equation:

$$\text{Log}_e\,[\alpha_0/\alpha_t] = \frac{k[B]t}{[A]}$$

where α_0 and α_t are, respectively, the initial optical rotation and the rotation after *t* seconds, $[B]$ is the concentration of ketone, and $[A]$ is the concentration of the alkoxide. Activation energies and entropies of activation were deduced. Interpretation of the results showed that they were consistent with the current theory for the reaction mechanism especially when the complex nature of aluminum alkoxides was taken into account. These authors also pointed out that the efficacy of aluminum alkoxides as reductants was due to their ability to coordinate with the carbonyl compound to a degree sufficient to allow the reaction to proceed at a reasonable speed. Strong coordination would simply produce a complex compound devoid of catalytic properties.

It seems likely that this moderate degree of coordination with other molecules is the property which confers on numerous metal alkoxides their catalytic behavior in other organic reactions—e.g., transesterification, alcoholysis, etc. McElvain and others (*114–116*) discovered that aluminum alkoxides would cause the dealcoholation of carboxylic orthoesters to ketene acetals and they proposed the following cyclic transition state for the reaction mechanism.



They found that the less polymerized aluminum derivatives—e.g., tertiary butoxide or isopropoxide—were more effective than the more highly polymerized methoxide or ethoxide and concluded that this was due to the greater ease of coordination of the former compounds with the orthoester.

It is an interesting feature of the metal alkoxides that they have little tendency to coordinate with other donor molecules and instead prefer to indulge in autocomplex formation. Among the large number of new alkoxides of titanium, zirconium, hafnium, cerium, thorium, niobium, tantalum, or uranium prepared in these laboratories in recent years, only the following complexes are known: $Ti(OBu^t)_4,Bu^tOH$; $Zr(OPr^i)_4,Pr^iOH$; $Ce(OPr^i)_4,Pr^iOH$; $Zr(OPr^i)_4,C_5H_5N$; and $Ce(OPr^i)_4,C_5H_5N$. As an alternative to autocomplex formation there is the characteristic formation of double alkoxides which was investigated by Meerwein and Bersin (*122*). These authors prepared more than fifty compounds which they formulated as alkoxy-salts—e.g., $K[Li(OC_3H_7)_2]$; $K_2[Be(OEt_4)]$; $Na_2[Mg(OC_3H_7)_4]$; $K[Zn(OEt)_3]$; $Li[Al(OEt)_4]$; $Ca[Al(OEt)_4]_2$; $Cu[Al(OEt)_4]_2$; $Na[Fe(OEt)_4]$; $NaH_3[Sn(OEt)_6]_2$; $CaH_6[Sn(OEt_6]_4$; $K_2Sn^{(II)}[Sn^{(IV)}(OEt)_6]$; $KH_3[Ti(OBu)_6]$; and $NaH[Zr(OEt)_6]$. In these compounds the more electropositive metal becomes the cation while the other metal becomes the central atom in the anion. These formulations were supported by titrations in anhydrous solvents using thymolphthalein indicator. Thus the alkoxides of aluminum,

boron, ferric iron, zinc, titanium, or zirconium behaved as acids and were sharply titrated with the appropriate basic alkoxide in accordance with the requirements of the double metal alkoxide formula. Meerwein and others (*120, 123*) also found that aluminum alkoxides catalyzed the diazomethylation of alcohols to ethers and this constituted further evidence for the acidic nature of the aluminum compounds. The stability of the double alkoxides involving aluminum was emphasized by the fact that these—e.g., $Na[Al(OEt)_4]$—compounds were inactive in the Meerwein-Ponndorf reduction of ketones because of the inability of the ketone to coordinate with the aluminum complex. Although the alkali metal aluminum alkoxides may well be ionic as their formulas suggest, the nature of such compounds as $Mg[Al(OEt)_4]_2$ and $Ca[Al(OC_3H_7)_4]_2$ seems to be in doubt. These compounds are not only soluble in organic solvents but they may be distilled unchanged, in marked contrast to the nonvolatile alkoxides of either magnesium or calcium which are also insoluble in organic solvents. Moreover, there is some doubt as to the formulation claimed by Meerwein and Bersin for the double alkoxides of zirconium. As previously mentioned, the author was unable to obtain any compounds of the type $M^{(I)}H[Zr(OR)_6]$ and found that zirconium ethoxide was neutralized with only one half an equivalent of sodium ethoxide as against the one equivalent reported by Meerwein and Bersin. The careful and detailed work of Bartley (*7*) in these laboratories has revealed the existence of stable neutral double alkoxides having the general formulas $M^{(I)}Zr_2(OR)_9$ or $M^{(II)}Zr_4(OR)_{18}$ and behaving as typically covalent compounds. The only other types of complex found were $LiHZr_2(OPr^i)_{10}$ and $M^{(I)}Zr(OR\text{-tertiary})_5$ with the further possibility of $M_2{}^{(I)}Zr(OR\text{-tertiary})_6$. It is indeed interesting that among the large number of double alkoxides of zirconium obtained by Bartley, not one conformed to the type $M^{(I)}H[Zr(OR)_6]$ found by Meerwein and Bersin. Recent work (still in progress) by Carter (*56*) shows that the double alkoxides of titanium also assume the formulas $M^{(I)}Ti_2(OR)_9$; $M^{(I)}Ti(OR)_5$; or $M_2{}^{(I)}Ti(OR)_6$.

Finally, a volatile double complex of aluminum and uranium has been reported (*2*). The new compound, $Al_4U(OPr^i)_{16}$, was prepared by means of the following reaction:

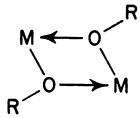
$$4Na[Al(OPr^i)_4] + UCl_4 \rightarrow Al_4U(OPr^i)_{16} + 4NaCl$$

It should be evident from this account that several aspects of the chemistry of metal alkoxides merit further attention. The author and others are at present engaged on studies of the catalytic behavior of metal alkoxides in the Meerwein-Ponndorf and related reactions, and a program on the thermal decomposition of metal alkoxides has been initiated.

Physical Properties

The metal alkoxides show a gradation in physical properties from the solid nonvolatile ionic compounds of the alkali metals through the weakly volatile polymeric covalent alkoxides of metals with valencies of three, four, or five to the monomeric covalent liquid alkoxides which are the most volatile. There is a paucity of information concerning the ionic alkoxides, although conductance measurements have shown that dilute solutions of sodium alkoxides are fully ionized in alcoholic solution (*103*). The insolubility and nonvolatility of magnesium alkoxides could be due to either ionization with a high lattice energy or alternatively to giant covalent molecules. On the other hand the essentially covalent nature of polymeric aluminum ethoxide is not in doubt, since Masdupuy and Gallais (*119*) have demonstrated that the molten compound has a negligible specific electrical conductance over a wide temperature range. More data are available on the covalent alkoxides which exhibit the characteristic structural properties of the metal atom concerned. In particular it seems highly probable that the polymeric nature of many of these compounds is due to covalency ex-

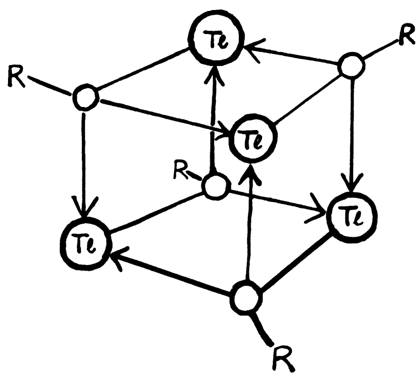
pansion by the metal which is involved in intermolecular bonds with oxygen from neighboring alkoxide groups:



I

Direct experimental confirmation of this hypothesis by x-ray diffraction is still awaited. Neither is the nature of the intermolecular bond clear. Although the covalent bond depicted above is possible, there is also the possibility, due to the polarity of the $\overset{\delta+}{M}$—$\overset{\delta-}{O}$ R primary bond, that the bonding is electrostatic in nature. For convenience in presenting certain structures, the covalent formulation is used in this text.

An interesting contrast between the alkali metals and univalent thallium is brought out by the alkoxides. Thus although these alkoxides are all nonvolatile and undergo reversible reaction with water, giving the basic hydroxide, yet the thallous alkoxides are soluble in nonpolar organic solvents. The covalent nature of thallous alkoxides was confirmed by the work of Sidgwick and Sutton (*157*), who found these compounds to be tetramers and proposed the structure:



The high stability of this unit is reflected in the nonvolatility of these derivatives and the fact that thallous ethoxide is tetrameric even in boiling ethyl alcohol. Experiments by the author (*26*) show that this structure is little affected by the shape of the alkyl groups, as the tertiary amyl oxide was found to be exactly tetrameric over a wide concentration range in boiling benzene.

During the past two decades many publications on the physicochemical properties of the alkoxides of aluminum (*126, 128, 150, 167*); titanium (*3, 38–41, 57–59, 65, 66*); zirconium (*38–41, 47, 48*); cerium (*29, 30*); thorium (*44, 46*); niobium (*28*); tantalum (*49–51*);and uranium (*2, 27, 82*) have appeared. As a result of systematic studies on the alkoxides of the Group IV metals, certain structural principles have emerged. Perhaps the most important principle concerns the stereochemical effect of the alkoxide group. The details of these deductions are given in the original papers and the review by Wardlaw (*169*), but it can be briefly stated that branching of the alkyl group causes steric hindrance to intermolecular association, thus causing a decrease in the degree of polymerization and an increase in volatility. This is illustrated in Table I by some results for the isomeric amyl oxides of zirconium (*39*).

The behavior of the neopentyloxide supports the view that this phenomenon is caused essentially by steric effects rather than the electronic inductive effects of the alkyl groups. This is because the neopentyl group exerts a powerful steric effect

Table I. Polymerization of Zirconium Oxides

R in $[Zr(OR)_4]_n$	B.P., °C./Mm. Hg	Degree of Polymerization, n
$Me \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot$	256/0.01	3.2
$Me_2CH \cdot CH_2 \cdot CH_2 \cdot$	247/0.1	3.3
$MeEtCH \cdot CH_2 \cdot$	238/0.1	3.7
$Me_3C \cdot CH_2 \cdot$	188/0.2	2.4
$MePr^nCH \cdot$	178/0.05	2.0
$MePr^iCH \cdot$	175/0.05	2.0
Me_2EtC	95/0.1	1.0

by virtue of its configuration but the electron-releasing tendency of its *tert*-butyl group is substantially blocked by the carbinol carbon atom. The alkoxides of aluminum, titanium, zirconium, hafnium, cerium, thorium, tin, niobium, tantalum, and uranium all show this chain branching effect in varying degrees and it is clearly of fundamental importance.

The second principle which has emerged from this work is that for metals of the same valency, the shielding requirements of the central atom are mainly determined by its atomic radius. For example, with the Group IV metals the smallest alkoxide groups to cause the formation of essentially monomeric tetraalkoxides were: Ti,Pr^i; $Zr(Hf),Bu^t$; $Ce^{(IV)},CMeEt_2$; and Th,CEt_3. Thus the smaller the central atom the smaller is the alkyl group required to shield it and this is entirely consistent with the stereochemical theory. This point is illustrated in Figure 1, where the volatilities of these metal alkoxides are grouped in relation to the size and branching

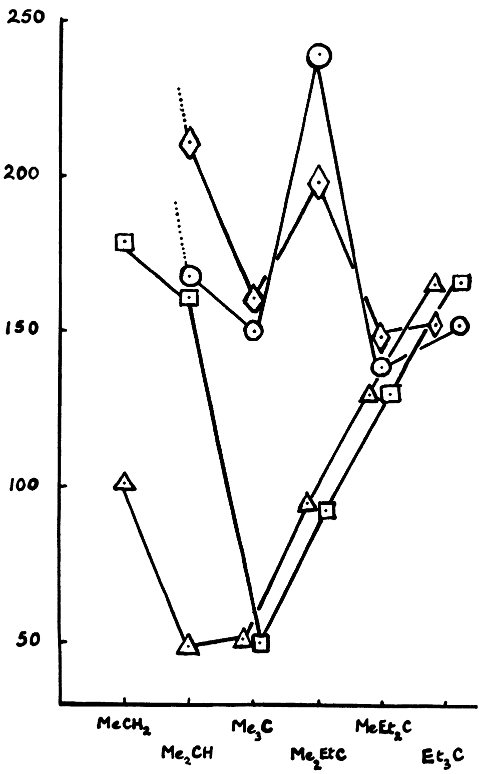


Figure 1. Volatilities of metal alkoxides

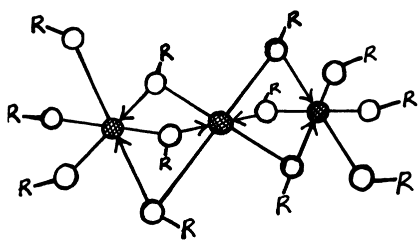
of the alkyl group. In addition the boiling points of the monomeric tertiary alkoxides of different metals are fairly close together and this suggests that the contributions to intermolecular forces from the metals are either equal, which seems very unlikely, or are effectively reduced by the screening effect of the organic groups. The latter view is supported by the results of vapor pressure measurements (*40, 42*) which show that analogous monomeric alkoxides of titanium, zirconium, and hafnium have the same latent heats of vaporization. This is illustrated in Table II by data on the tertiary amyl oxides, where $T_{5.0}$, L_v, and $\Delta S_{5.0}$ are the boiling point (°C.), heat of vaporization (kcal./mole) and entropy of vaporization (cal./deg./mole) at 5.0 mm. of mercury pressure.

Table II. Data for Tertiary Amyl Oxides

M in $M(OCMe_2Et)_4$	$T_{5.0}$	L_v	$\Delta S_{5.0}$
Ti	142.7	16.7	40.0
Zr	138.4	16.3	39.5
Hf	136.7	16.3	39.8

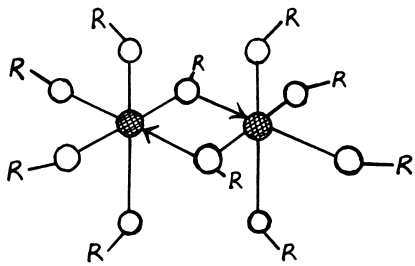
An interesting feature of Table II is that the boiling points, although close together, are definitely in the order Ti > Zr > Hf, which is exactly the reverse of the order of molecular weights. The theoretical explanation for this has been considered by the author (*25*), and is outside the scope of this article, but the effect is of importance in connection with the possibility of separating metals by distillation of their alkoxides. It appears that monomeric alkoxides of approximately the same size —i.e., number of carbon and hydrogen atoms—and shape will have very similar boiling points. For example, tantalum penta-*tert*-butoxide, $TaO_5C_{20}H_{45}$ (boiling point 149.5° at 5.5 mm.), resembles titanium tetra-*tert*-amyl oxide, $TiO_4C_{20}H_{44}$ (143° at 5.0 mm.), in volatility and the titanium derivative is also very close in boiling point to the tetra-*tert*-amyl oxides of zirconium and hafnium. Similarly for some of the higher monomeric alkoxides: $Ti(OCMeEt_2)_4$ boiling point, 128° at 0.1; $Zr(OCMeEt_2)_4$ 130° at 0.1; $Ti(OCHEtPr^n)_4$ 134° at 0.1; $Ti(OCHMeBu^n)_4$ 126° at 0.1; $Ti(OCHMeBu^t)_4$ 127° at 0.1; $Zr(OCHMEBu^t)_4$ 128° at 0.1; $Ta(OCHMePr^i)_5$ 137° at 0.1; and $Ta(OCMe_2Et)_5$ 139° at 0.1. This last group includes both secondary and tertiary alkoxides.

According to the author, there may be another general principle applicable to the covalent metal alkoxides—namely, that an alkoxide undergoes the minimum degree of polymerization consistent with the attainment of the maximum covalency of the metal. This is well illustrated by the behavior of titanium tetraethoxide. The cryoscopic measurements of Caughlan and others (*59*) in benzene showed that the degree of polymerization of titanium ethoxide increased with the concentration to a limiting trimeric state. These authors proposed two similar structural models for the trimer; one of these is illustrated.



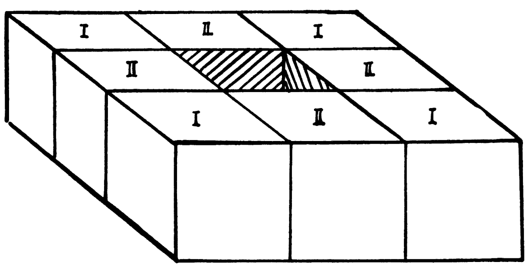
In this model, each titanium atom exhibits its maximum covalency of 6 in approximately the octahedral configuration. However, the covalency maximum could

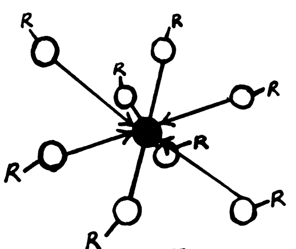
still be observed with higher polymers also with octahedral titanium but with bridging across edges of the octahedra instead of faces. This does not appear to be the case, since the trimeric unit is evidently preferred. Similarly the studies on the alkoxides of niobium (*49*) and tantalum (*28*) showed that these compounds never exceeded dimerization and the structure:



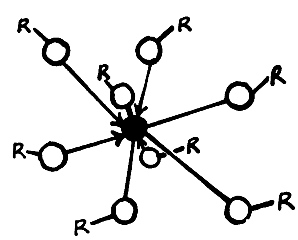
was accordingly proposed. In this case the covalency of 6 is achieved by bridging involving a common edge for the octahedra, although the octahedral configuration could have been maintained in higher polymers involving the sharing of apices.

The elements zirconium, cerium(IV), and thorium are especially interesting because although they each exhibit a maximum covalency of 8, they also frequently assume the 6-covalent state. The smallest unit for an $M(OR)_4$ compound with 8-covalent M appears to be the arrangement shown:





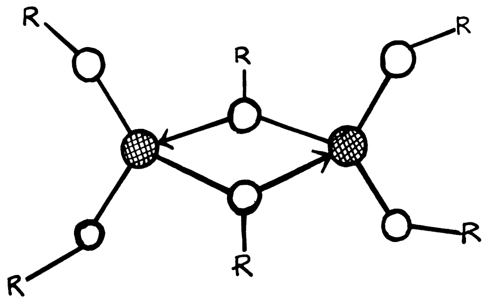
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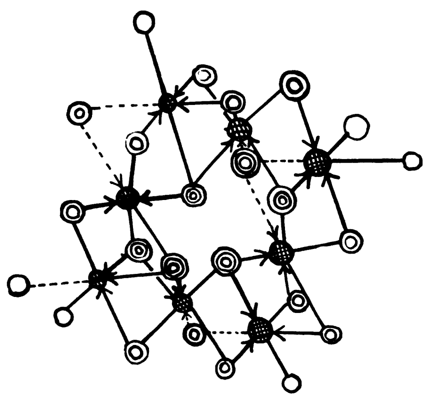
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of eight cubes in which there are two kinds of cube, the corner cube (I) and the side cube (II). The configurations of these cubes are shown in the inset. Hence it follows that the maximum complexity should be 8. It is unfortunate that the methoxides of zirconium, cerium(IV), and thorium are insoluble, because these would be likely to give the maximum degree of polymerization. However, the normal butoxides are soluble and the molecular weights in boiling benzene gave the values 3.4, 4.2, and 6.4, respectively, for the degrees of polymerization. Thus these metals appear to be exhibiting both 6- and 8-coordination and it is in line with the author's stereochemical theory that the metal with the largest atomic radius gives the highest pro-

portion of the maximum covalency and vice versa. It is obvious that the steric effect of the alkyl group will also control the tendency of the metal to exert its maximum covalency. For example, zirconium is probably 6-covalent in both the tetraisopropoxide which is trimeric and the solvate $Zr(OPr^i)_4,Pr^iOH$ which is dimeric. The latter is isostructural with the dimeric pentaalkoxides with the fifth group made up by the coordinated alcohol. Similarly several secondary alkoxides of cerium were shown to be trimeric (*30*). It is interesting to extend these principles to the aluminum alkoxides. Here is a tervalent metal which has a pronounced tendency towards the covalency of 4 and can exhibit a maximum covalency of 6. The smallest trialkoxide involving a 4-covalent metal will be dimeric:

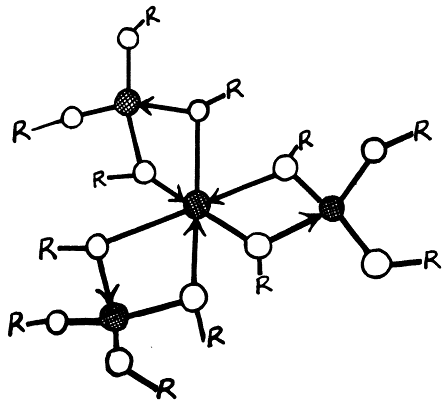


with the tetrahedral configuration for aluminum. Assuming the octahedral configuration for 6-covalent aluminum the author suggests that the octameric model:

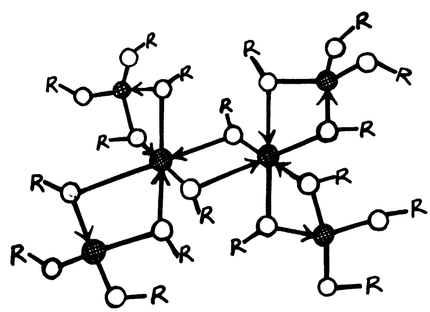


represents the minimum polymer. Therefore it would be predicted that aluminum alkoxides should not exceed 8-fold polymerization. In fact, the numerous studies on these compounds (*114, 126, 128, 150, 167*) have not revealed a polymerization greater than sixfold, while the tertiary butoxide is dimeric. Mehrotra (*126, 128*) has recently made a systematic study of the aluminum alkoxides and suggests that the discrepancies between the results published by different authors may be due to an "aging" effect. Thus he found that aluminum isopropoxide was tetrameric after storage for 2 months, whereas the redistilled product was trimeric, and McElvain and Davie (*114*) gave a value of 5 to 6 for the degree of polymerization for this compound. It is tempting to suggest that the aging effect is really caused by the tendency of aluminum to increase its coordination number from 4 to 6. Thus the freshly distilled sample will be largely in the 4-covalent state but will slowly undergo the structural rearrangement necessary for assuming the 6-covalent state. Moreover, Mehrotra (*128*) has found

that the isopropoxide is dimeric even in the vapor state, which is in accord with the above proposition. Both Mehrotra (*128*) and Robinson and Peak (*150*) found that several primary alkoxides of aluminum were tetrameric. This is exactly in agreement with the structural model:

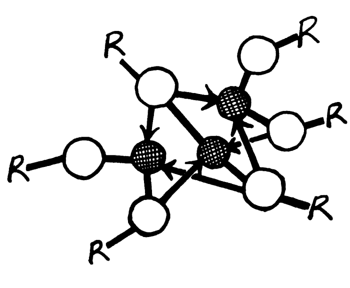


in which the central aluminum is octahedrally 6-covalent and the remaining three aluminums are tetrahedrally 4-covalent. Similarly there is shown another possible structure in which one third of the aluminum is 6-covalent in a 6-fold polymer:



Hence the key polymers in the aluminum alkoxides should be the dimer, tetramer, hexamer, and octamer, but because average molecular weights are experimentally determined, the actual degree of polymerization calculated will depend on the relative proportions of the different key polymers.

Applying the principle of minimum polymerization to the bivalent metals leads to the prediction that the dialkoxide of a metal which increases its covalency from 2 to 4 should be trimeric as shown:



which features tetrahedral coordination of the metal. On the other hand, covalency expansion to 6 would involve the formation of a giant polymer. Beryllium alkoxides should conform to the first proposition, because beryllium has a pronounced tendency towards covalency and is limited to the maximum covalency of 4 with the tetrahedral configuration. Beryllium ethoxide has been made (*156*) but its molecular weight is not known. It is also clear that thallous alkoxides adhere to the above principle. The unusual covalency change of thallium from 1 to 3 is due to the inert $6S^2$ pair of electrons leaving the three $6p$ orbitals available for bonding in precisely the directions demanded by Sidgwick and Sutton's model.

Although some of these arguments may appear speculative, they have been very successful in interpreting some unexpected features of the hydrolysis products of metal alkoxides.

Hydrolysis of Metal Alkoxides

Most of the metal alkoxides are readily hydrolyzed in the presence of an excess of water to give the metal hydroxide and ultimately the oxide. From the viewpoint of industrial applications it is essential to know more about the intermediate stages between the metal alkoxide and its ultimate hydrolysis product—whether the products of partial hydrolysis are hydrolyzed as rapidly as the original alkoxide. Also it is desirable to find whether or not the hydrolysis reaction is catalyzed by some compounds and inhibited by others. In particular, the possibility of controlling the rate of hydrolysis must be investigated. Attention has hitherto been mainly directed to the study of titanium alkoxides, probably because the titanium compounds, especially the butoxide and isopropoxide, are most used in industry at present.

Prior to 1951 there is only one reference to the hydrolysis products of titanium alkoxides. Bischoff and Adkins (*11*) pointed out that titanium tetraethoxide was a liquid and that the crystalline compound obtained by Demarcay (*69*) was a hydrolysis product. Recent work (*35, 57*) has revealed that titanium tetraethoxide is in fact a crystalline compound and that the product obtained by Bischoff and Adkins was the supercooled liquid.

In 1951, Winter (*173*) reported the preparation of the titanium oxide butoxide, $Ti_2O(OBu^n)_6$, by hydrolysis of the tetranormal butoxide. In the same year Cullinane and others (*66*) described results obtained during the hydrolysis of alcoholic solutions of several alkoxides of titanium. In the case of the ethoxide and the n-propoxide they isolated solids whose composition agreed with the metatitanate formula, ROTiO(OH), but the n-butoxide was noticeably slower to hydrolyze. At about the same time Boyd (*16*) reported a more detailed investigation of the hydrolysis of titanium alkoxides. He concluded that titanium alkoxides were hydrolyzed much more rapidly than the corresponding alkyl orthosilicates and that the partially hydrolyzed alkoxides rapidly reacted with the tetraalkoxide to produce new compounds of intermediate degrees of polymerization. Polymers containing higher alkyl groups were obtained by alcohol interchange with the more readily obtained polymers of lower alkoxides. With titanium butoxide, the addition of water in the ratio $(h) =$ moles of water: atoms of titanium, of up to 1.20 caused quantitative hydrolysis while for $(h) = 1.20$ to 2.25 only about 1.4 to 1.5 moles of water per titanium atom were consumed, suggesting that hydrolysis becomes more difficult as the degree of hydrolysis becomes greater. With $(h) = 3.0$ precipitation of titanium dioxide occurred. In the range $(h) = 0$ to 1.0, Boyd suggested that essentially linear polymers are formed with some chain branching but no cross linking in accordance with the following mechanism:

$$n\text{-Ti(OR)}_4 + (n-1)\text{H}_2\text{O} \rightarrow (\text{RO})_3\text{Ti—O—[Ti(OR)}_2\text{—O]}_{n-2}\text{—Ti(OR)}_3 + 2(n-1)\text{ROH} \quad (19)$$

This system leads to the relationship $n = 1/[-(h)]$, where n is the degree of polymerization and agreement with experiment was found for $n = 1$ to 6. The com-

pounds produced in the reactions involving $(h) = 0$ to 1.0 varied in nature from viscous liquids to waxy solids. This work was followed by an important investigation by Minami and Ishino (*131*), who studied the hydrolysis of titanium butoxide both in solution in butyl alcohol and also by exposure of the tetraalkoxide to moist air. In solution attention was concentrated on the systems involving $(h) = 0.5$, 1.0, or 1.5. For each initial concentration of water, the rate change of viscosity of the solution was followed at the separate temperatures: 20°, 40°, 60°, and 80°C. In each experiment the initial rate was rapid and was followed by a slow approach over 7 to 8 hours to an apparent equilibrium. In particular the equilibrium position was dependent on the temperature. The authors concluded that hydrolysis was a two-stage process:

$$n\text{-Ti(OBu)}_4 + 4n\text{-H}_2\text{O} \rightarrow n\text{-Ti(OH)}_4 + 4n\text{-BuOH} \quad (20)$$

$$n\text{-Ti(OH)}_4 \rightarrow (\text{TiO}_2)_n + 2n\text{H}_2\text{O} \quad (21)$$

The initial hydrolysis (*20*) was believed to be rapid and possibly reversible, and the condensation (*16*) was considered the slow stage. Studies on the hydrolysis of the tetrabutoxide in moist air led to the interesting conclusion that the fourth butoxide group in $Ti(OBu)_4$ is considerably resistant to hydrolysis and this is consistent with the previous work of Boyd. Ishino and Minami also analyzed the products caused by hydrolysis at 80°C. and found that for $(h) = 1.5$ hydrolysis was incomplete. Cryoscopic molecular weight determinations (extrapolated to infinite dilution) were approximately in accordance with the formulas:

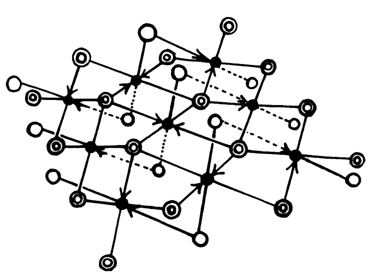
$$[\text{Ti}_2\text{O(OBu)}_6]_{1.5}, \quad [\text{TiO(OBu)}_2]_{2.2}, \quad \text{and} \quad [\text{TiO}_{1.44}(\text{OBu})_{1.22}(\text{OH})_{0.07}]_7$$

whereas Boyd's Equation 19 requires: $Ti_2O(OBu)_6$ and $[TiO(OBu)_2]_\alpha$.

In these laboratories the hydrolysis of several titanium and zirconium alkoxides has been studied. It was found that titanium tetraethoxide (*35, 36*) underwent rapid and complete hydrolysis in ethyl alcoholic solution and the crystalline compound $Ti_6O_4(OEt)_{16}$ was precipitated in the early stages $[(h) < 1.0]$. Ebulliometric studies showed that Equation 19 was inapplicable to this system whereas reasonable agreement up to $(h) \sim 1.2$ was found with the relation:

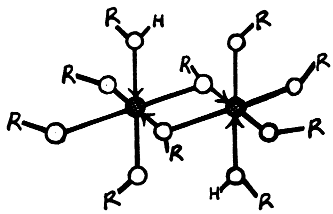
$$n = \frac{12}{4 - 3(h)} \quad (22)$$

This applies to a system of compounds having the general formula $Ti_{3(x+1)}O_{(4x)}(OEt)_{4(x+3)}$ and valid for $(h) = 0$ to 1.33. The compounds $Ti_6O_4(OEt)_{16} (x = 1)$ and $[TiO(OEt)_2]_{12} (x = 3)$ have been isolated and their molecular weights are in agreement with these formulas while the tetraethoxide corresponds to $x = 0$. These compounds mark the early stages in the formation of the infinite trilinear polymer:

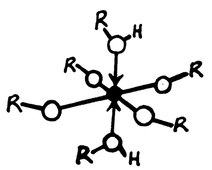


This structure is based on that of the trimeric ethoxide and is formed by joining up the trimeric units through Ti-O-Ti bridges. The ultimate high polymer has the formula $[Ti_3O_4(OEt)_4]_\alpha$ and it is noteworthy that addition of water in the region

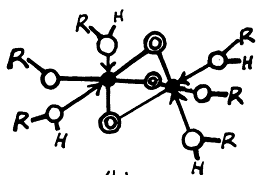
$(h) = 1.5$ to 2.0 gave insoluble products whose analyses were near that of the infinite polymer. Similarly, the action of heat on $Ti_{12}O_{12}(OEt)_{24}$ under reduced pressure brought about disproportionation and gave the volatile tetraethoxide and the nonvolatile infinite polymer: $Ti_{12}O_{12}(OEt)_{24} \rightarrow 3[Ti_3O_4(OEt)_4]_a + Ti_3(OEt)_{12}$. It seems significant that insoluble nonvolatile products with compositions near to $Ti_3O_4(OR)_4$ were also obtained in the hydrolysis of the isopropoxide, tertiary butoxide, and tertiary amyl oxide. Ebulliometric studies on the hydrolysis of the *n*-propoxide and isobutoxide revealed rapid reactions, but the degrees of polymerization did not agree with the requirements of Equation 22. The observed values of n were considerably less than theory, as indeed was the case for the ethoxide for $(h) > 1.2$. It is believed that this is due to depolymerization of the oxide alkoxides in the higher boiling solvents with the formation of solvated lower polymers. Thus it was suggested (*36*) that there are three fundamental structural models for the titanium oxide alkoxide polymers. The first model is based on the trimer while the second model is based on the solvated dimer $Ti_2(OR)_8$, $(ROH)_2$:



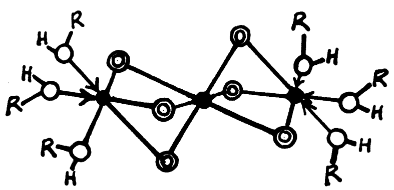
The third system contains only three structures:



(a)



(b)



(c)

and is based on a monomeric tetraalkoxide. The unifying feature of all three structural models is the adherence to 6-coordinate titanium which is regarded as the key point in the theory. The equations for Models II and III are:

$$\text{Model II} \qquad n = \frac{6}{3 - 2(h)}$$

$$\text{Model III} \qquad n = \frac{3}{3 - (h)}$$

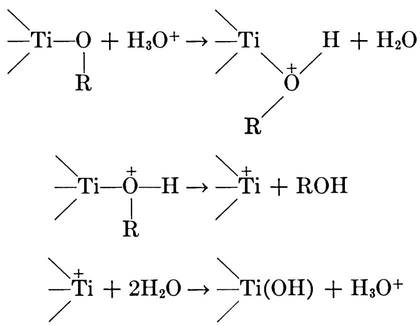
By allowing for solvation according to these systems the results for the *n*-propoxide (mainly Model II) and isobutoxide (mainly Model III) were in much better agreement with the theory. A similar improvement was obtained for the ethoxide. These postulated structures are idealized and apply to the behavior of these compounds in boiling alcoholic solutions and will not necessarily be valid for reactions occurring under different conditions. Ebulliometric experiments on the *sec*-butoxide, *n*-butoxide, *tert*-butoxide, and *tert*-amyl oxide gave interesting results. The hydrolysis of the *sec*-butoxide occurred at a measurable rate which was increased by traces of acid and decreased by traces of alkali. This behavior may well be caused by the steric effect of the branched butyl groups which would be expected to oppose nucleophilic attack by hydroxyl ions on the titanium (Equation 23a) in the alkaline system.

(a) $$Ti(OR)_4 + OH^- \rightarrow Ti(OH)(OR)_3 + OR^-$$

(b)

(c)

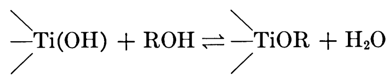
(d)



(23)

On the other hand, the acid-catalyzed mechanism depicted in Equation 23b, c, and d will not be appreciably affected by the steric factor.

In experiments with the *n*-butoxide it was demonstrated that the hydrolysis was incomplete even for values of (*h*) as low as 0.5. Moreover, the very small degree of polymerization found in boiling butanol for (*h*) as high as 6 suggests that stable hydroxyl-titanium bonds are present. An equilibrium system of the following type:



may well explain the unusual features in the hydrolysis of the *n*-butoxide. It is also likely that relatively stable Ti-OH bonds are produced during the hydrolysis of the tertiary alkoxides, although attempts to isolate a hydroxy compound were unsuccessful. The results suggested that the initial step

$$Ti(OR)_4 + H_2O \rightarrow Ti(OH)(OR)_3 + ROH$$

and also the condensation step

$$Ti(OH)(OR)_3 + Ti(OR)_4 \rightarrow (RO)_3Ti{-}O{-}Ti(OR)_3 + ROH$$

were both slower than the subsequent hydrolysis of $Ti(OH)(OR)_3$, $Ti(OH)_2(OR)_2$, and $Ti(OH)_3(OR)$ where R is a tertiary alkyl group. Thus in the ebulliometric hydrolysis of the *tert*-butoxide the first addition of water $(h) < 0.1$ caused the deposition of an insoluble compound and the experiment was discontinued. With the *tert*-amyl oxide the titanium compound remained monomeric throughout the experiment [final value of $(h) = 3.0$]. Other recent work on the hydrolysis of titanium alkoxides includes that of D'Adamo and Kienle (*68*), who found that neopentyl alcohol was recovered by the hydrolysis of titanium neopentyl oxide, thus showing that the titanium-oxygen bond is disrupted and not the carbon-oxygen bond. Nesmeyanov and others (*135*) have isolated the following compounds: $(EtO)_8Ti_3O_2$ and $(RO)_3TiOTi\ (OR)_3$ where $R = Et$, Pr^n, or Bu^n.

The paper by Bistan and Gomory (*12*) confirmed the conclusions of previous workers that the hydrolysis of the butoxide is incomplete in the later stages and they showed that this effect is even more marked in the hydrolysis of other titanium alkoxides and aryloxides—e.g., heptyl, cetyl, benzyl, phenyl, and *m*-cresyl derivatives. Some of their results are quoted in Table III.

Table III. Results of Bistan and Gomory

R in $Ti(OR)_4$	(*h*)		
	Added	Recovered	Consumed
n-Butyl	0.5	—	0.5
	1.0	—	1.0
	2.0	0.47	1.53
n-Heptyl	0.5	0.04	0.46
	1.0	0.07	0.93
	2.0	0.52	1.48
Cetyl	0.5	0.07	0.43
	1.0	0.08	0.92
	2.0	0.55	1.45
Benzyl	0.5	0.04	0.46
	1.0	0.16	0.84
	2.0	0.69	1.31
Phenyl	0.5	0.12	0.38
	1.0	0.14	0.86
	2.0	0.83	1.17
m-Cresyl	0.5	0.09	0.41
	1.0	0.17	0.83
	2.0	0.82	1.18

Present knowledge of the hydrolytic reactions of titanium alkoxides may then be summarized as follows. The rapidity and completeness of the hydrolysis depend on the size of the alkyl group; hydrolysis is slower and less complete the higher the alkyl group. It is particularly slow for the higher homologs after the removal of three quarters of the available alkoxide groups and it is possible that relatively stable Ti-OH groups are present in alcoholic solution and that an equilibrium is established between hydrolysis and esterification. In all cases the degree of polymerization in the early stages of hydrolysis is very small and for the lower alkoxides this may be a consequence of the tendency of titanium to exhibit the coordination number 6 in compact structures. In no case does the polymerization resemble the characteristic behavior of silicon in the formation of silicones. Another general feature of the partial hydrolysis products of titanium alkoxides is their tendency to disproportionate when heated and to produce the volatile tetraalkoxide and a more highly polymerized nonvolatile residue. These properties all suggest that the Ti-O bonds in the alkoxides are relatively weak and the ultimate product of hydrolysis is titanium dioxide. It is clear that only a small beginning has so far been made in the studies of the hydrolysis of metal alkoxides and interesting developments are anticipated in the near future.

Industrial Applications of Metal Alkoxides

A survey of the recent literature reveals a rapid increase in the industrial importance of metal alkoxides. In particular, titanium alkoxides are being produced on an ever-increasing scale. For example, the manufacture and sale of titanium butoxide has been doubled in Britain during the last year, while in the United States the output of titanium alkoxides was quadrupled during 1955. The output of the products can now be reckoned in tons per annum.

The origin of this remarkable development in titanium chemistry may be traced to 1947 when Kraitzer, McTaggart, and Winter (*109*) reported that titanium butoxide could be used in making heat-resistant paints. Another important impetus occurred in 1950 when Speer and Carmody (*161*) announced that titanium alkoxides conferred

water-repellent properties on textile fabrics, leather, wood, and other materials. Since then the alkoxides of titanium and other metals have been used increasingly in these and other related applications.

Heat-Resistant Paint

Following their original work in 1947, Winter and others (*14*, *62*, *63*, *109*, *173*, *174*) have published a series of articles on the uses of titanium alkoxides in heat-resistant paints. They have shown that the partially hydrolyzed butoxide may be used in place of the tetrabutoxide and that the chloride content of the titanium compound should be kept below 0.005%; otherwise corrosion will occur due to the formation of hydrochloric acid. Contributions to this field have also come from other authors, notably Rozan (*153*), Hancock and Sidlow (*87*), Thomas (*162*), and Sidlow (*158*, *159*). The heat-resistant titanium paint is usually composed of titanium tetrabutoxide (or a partial hydrolysis product), aluminum powder pigment, and a solvent such as white spirit (industrial solvent, petroleum fraction). According to Sidlow (*158*, *159*) the relative proportions of titanium butoxide and aluminum are critical for the formation of a coating with optimum heat and corrosion resistance. It appears that the function of the titanium alkoxide is to produce titanium dioxide under conditions in which it will bond together the protected surface—e.g., steel—and the aluminum pigment. Such coatings are then stable for prolonged periods at 600°C. which is near to the melting point of aluminum.

These coatings are most efficient under conditions of continuous high temperature—i.e., low humidity—while under more humid conditions corrosion may occur because of the porous nature of the coating. Cox and Winter (*62*) have improved the corrosion resistance by incorporating zinc metal pigment in place of the aluminum, but the gain in corrosion resistance is offset by a loss in heat resistance and maximum operating temperature for the zinc-titanium paint appears to be about 400°C. (melting point of zinc, 418°C.). The same authors are investigating the possibility of using titanium alkoxides in antifouling paints for marine use.

The suitability of titanium butoxide as a paint medium is closely linked to its hydrolytic properties. Although all titanium alkoxides are ultimately hydrolyzed to the dioxide and could in principle be used in heat-resistant aluminum-titanium paints, the lower alkoxides are so rapidly hydrolyzed by even traces of water that they would not produce stable paint media. On the other hand, the less reactive higher alkoxides hydrolyze more slowly and the drying of the paint would then be impeded. With titanium butoxide the initial rate of hydrolysis is rapid but the products are soluble, so that a stable paint medium is possible. Further hydrolysis to insoluble products is slower but it still occurs at a reasonable rate when a film of the paint is exposed to the atmosphere. The ultimate formation and bonding of the titanium dioxide probably occur when the coating is heated in air.

Another use for titanium butoxide was foreshadowed by Cox and Winter (*62*). They suggested that a medium containing mica and the butoxide would give a coating with good high temperature insulating properties. Considerable quantities of titanium butoxide are now being manufactured for the production of heat-resistant paint and it will be interesting to see whether the alkoxides of other metals such as zirconium, thorium, niobium, or tantalum will find similar applications. Another possibility is the incorporating of metals other than aluminum as pigments in order to raise the maximum operating temperature above 600°C.

Water Repellency

The use of metal alkoxides as water-repellent agents has developed rapidly since the paper by Speer and Carmody (*161*). The problem facing the chemist is that of producing agents which will confer permanent water-repellent properties on various

materials. Thus the water repellency of a treated textile fabric must not be impaired by repeated laundering, and water-repellent leather footwear must be capable of withstanding the effects of weathering. Sidlow (*158*) suggests that titanium alkoxides on their own are more suitable for the waterproofing of leather rather than textiles. The literature contains many claims for the waterproofing properties of many titanium alkoxides, oxide alkoxides, or acylates (*4, 5, 18, 20, 84, 111*). Zirconium alkoxides have also been tested and Mailander (*118*) claimed that solutions containing 0.1 to 0.3% of zirconium ethoxide and 1.0 to 10% of petroleum wax, petrolatum, or polymerized octadecyl vinyl ether in aromatic or halogenated aliphatic solvents would impart water repellency to textiles. Other alkoxides of zirconium and of aluminum were also effective in similar preparations (*118*).

The water-repellent properties of the silicones are well known and it was not surprising that mixtures of silicones and metal alkoxides should be tested. Tsukada and Tsuji (*166*) found that a solution containing 2.5% of silicone and 0.2% of aluminum ethoxide in benzene rendered textile fibers water-repellent. Similarly, it has been claimed that mixtures of silicones and titanium alkoxides in petroleum solution are suitable for waterproofing leather (*67*) and textiles (*132*). Silicone-zirconium alkoxide preparations have also been used for the same purposes (*87*). Boyd (*15, 22*) prepared liquid copolymers by the partial hydrolysis in benzene solution of alkyl alkoxyl silanes in the presence of titanium alkoxides, acylates, or alkylamides. These copolymers were used for waterproofing textiles.

A most interesting feature of the silicone–metal alkoxide water-repellents is that they are more effective than either the silicone or the metal alkoxide alone. It is known that metal alkoxides cause the final "curing" of silicones to occur at 50° to 80°C. instead of the normal temperature of 200° to 250°C. required by the silicone. In this connection the metal alkoxide probably hastens the polymerization process by reactions involving the alkoxide and the Si-OH groups which cause cross linking to occur. However, the enhancement of water-repellent properties may be due to additional factors besides this silicone-curing effect. Thus the silicones with the best waterproofing properties are those containing some Si-H groups (*151*) and it may be that the metal alkoxides interact with these Si-H groups. Moreover, metal alkoxides are waterproofing agents in their own right, presumably because of interaction with fibers. Therefore it seems possible that in addition to the curing effect, the metal alkoxides may interact with both fiber and silicone and thus act as a bonding agent. Other organic compounds of metals—e.g., 2-ethyl hexoate—enhance the water-repellent properties of silicones (*24*), so that this effect is not specific to metal alkoxides.

Paint Driers and Modifiers

Metal alkoxides are now being used to accelerate the drying of paints (*9, 23, 60, 61, 154*). In general, larger proportions of metal alkoxide are incorporated compared with the usual proportions of metal naphthenates but the alkoxide improves the quality of the coating in addition to accelerating the drying process. It is believed that the metal alkoxide reacts with the hydroxyl groups in the paint medium, thus causing cross linking and polymerization. This property has been utilized in the modification of paints and lacquers (*104, 147, 149, 165, 172*). In particular, the cellulose ester films are considerably improved in heat and solvent resistance and also in mechanical properties (*8*). The lower alkoxides of titanium cause immediate gelation and this effect is obviated either by using a solution of the alkoxide in its own alcohol or by incorporating a less reactive complex alkoxide (*75, 155*). The hydrolytic properties of the titanium alkoxides are again seen to be the dominating factor in the control of a valuable process. The less reactive complex alkoxides are derived from chelating hydroxy compounds such as 1:3 diols—e.g., octylene glycol—ketoalcohols—e.g., diacetone alcohol—or easily enolizable derivates—e.g., β-diketones or β-ketoesters. It is probable that in some of these monomeric compounds the titanium is exerting its

maximum covalency and this factor coupled with the stability of chelate rings renders the titanium much less vulnerable to nucleophilic attack by the oxygen of hydroxyl groups and thus accounts for the lower reactivity.

Other Applications

The silicone–metal alkoxide copolymers are also used as film-forming media (*1, 6, 73, 108*). Gulledge (*86*) claims that the "titanated organosiloxane" polymers produce hard coatings which are opaque to ultraviolet light and suitable for incorporation in refrigerator enamels.

Another use for the less reactive titanium alkoxides is as adhesion promoters (*13, 70*). A thin adherent film of titanium dioxide is formed by the evaporation and slow hydrolysis of dilute solutions of the titanium alkoxides. This layer of titanium dioxide can be produced on surfaces of a wide variety of materials and it promotes the adhesion of paints and lacquers which would not otherwise stick. Boyd (*19*) claims that good adhesive compounds are obtained by modifying aminoplast resins through the incorporation of polymerized titanium alkoxides, acylates, or amides.

An interesting application of titanium or zirconium alkoxides is in the rapid drying of printing inks (*88*). Addition of the metal alkoxide to the wet print causes rapid drying due to interaction of the alkoxide with hydroxy compounds in the ink.

It is clear that the characteristic properties of metal alkoxides lead to considerable versatility in their applications and it is common to find that a given metal alkoxide preparation is claimed to be useful in several different applications.

In addition to the examples already cited, metal alkoxides are also finding other uses such as: polymerization catalysts (*176*), mordants (*17*), sizing agents (*18*), dispersing and antisludging compounds (*4, 13, 111*), dielectrics (*165*), catalysts in polyester formation (*53–55*), catalysts in transesterification (*143, 144*), and components in enamels (*152*). The metal alkoxides are also suitable for preparing pure metal oxides or highly "active" oxides (*85, 95, 96, 106*). According to Kearby (*105*) the aluminum alkoxides may be used to reduce the aldehydes produced in the Oxo process and, after hydrolysis and separation of the alcohols, an "active" alumina is also obtained. A novel use for titanium alkoxides is in the preparation of barium titanate (*76*).

There is the future possibility that metal alkoxides may be utilized in the separation and purification of metals. In this case the physical properties of the alkoxides will be brought into play, for it has been demonstrated that the volatility of a metal alkoxide is controlled by the size and shape of the alkyl group. Work is already in progress in these laboratories on the separation of zirconium and hafnium by the fractional distillation of their alkoxides. In this particular case, one is probably dealing with the most difficult example to choose for a metal alkoxide separation owing to the proximity of boiling points of the components (boiling point difference of about 1° to 2°C.). However, preliminary results (*170*) show that the method works and holds promise for large scale operations. This could be important in the atomic energy program, which requires hafnium-free zirconium. Among other systems being studied is the separation of niobium and tantalum by fractional distillation of their alkoxides and this should be considerably easier than the zirconium-hafnium separation. The distillation of uranium pentaethoxide has been patented as a means of enriching the uranium-235 isotope (*52*). An advantageous feature of the alkoxide separation is the readiness with which the metal alkoxide can be hydrolyzed to give the pure oxide and the alcohol. This should be of special importance where the pure metal is produced by reduction of the oxide and it should also be possible to recover and recycle the alcohol.

The metal alkoxides are being applied industrially on an ever-increasing scale and it seems likely that this expansion will continue in the future as the wide potentialities of these compounds are further developed.

Acknowledgment

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Metal Chelates

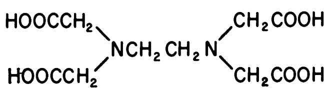
MARTIN KNELL

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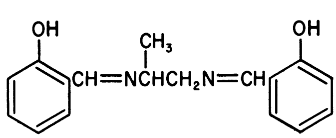
Metal chelates, in which an organic molecule bonds a metal cation covalently or ionically, are discussed. There are both synthetic chelates such as the phthalocyanines and natural chelates such as the porphyrins. The formation, stability, and commercial importance of these are summarized. The major uses of metal chelates are in agriculture and the dye and pigment industries.

A metal chelate is a compound in which a metal cation is bound by a molecule containing two or more sites for bond formation. The word chelate is derived from the Greek word *chela,* meaning claw, because of the structure of the molecules. A great variety of organic and inorganic molecules can participate in chelation. Only those chelates in which the chelating agent, or ligand, is organic are discussed here. In metal chelates, the metal is bonded either ionically or covalently with the strongly nonmetallic elements of Groups V and VI, whereas in other organometallics the metal is bonded covalently directly to carbon.

Most of the metal chelates produced in industry today are formed *in situ* and never isolated. By chelating metals in solution, undesirable properties such as precipitation of heavy metal soaps and hydroxides and catalysis by metallic ions can be avoided. The use of (ethylenedinitrilo)tetraacetic acid (EDTA) in the textile industry is well



known. Several million pounds are used each year in such operations as dyeing, kier boiling, and bleaching. In the latter operation, the chelating agent has a stabilizing effect on hydrogen peroxide, the decomposition of which is catalyzed by trace quantities of such metals as iron, copper, and manganese. Another chelating agent that has reached commercial importance as a result of its deactivating effect on trace quantities of a metal is *N,N'*-disalicylidine-1,2-propanediamine. This compound is sold



at the rate of about a million pounds per year and is added to gasoline to counteract the oxidative effect of trace quantities of copper which may be present in the gasoline.

Formation

An example of metal chelate formation is the reaction of EDTA with calcium. EDTA with four carboxyl groups ionizes in four steps, with four corresponding ionization constants:

$$H_4Y \rightleftharpoons H_3Y^- + H^+ \qquad k_1 = \frac{[H^+][H_3Y^-]}{[H_4Y]}$$

$$H_3Y^- \rightleftharpoons H_2Y^{-2} + H^+ \qquad k_2 = \frac{[H^+][H_2Y^{-2}]}{[H_3Y^-]}$$

$$H_2Y^{-2} \rightleftharpoons HY^{-3} + H^+ \qquad k_3 = \frac{[H^+][HY^{-3}]}{[H_2Y^{-2}]}$$

$$HY^{-3} \rightleftharpoons Y^{-4} + H^+ \qquad k_4 = \frac{[H^+][Y^{-4}]}{[HY^{-3}]}$$

where Y represents the (ethylenedinitrilo)tetraacetate anion.

These ionization constants have been determined (*4*), and expressed in terms of pk (log *k*) are $pk_1 = 1.99$, $pk_2 = 2.67$, $pk_3 = 6.16$, and $pk_4 = 10.26$. The titration of EDTA with an alkali is shown by curve *A*, Figure 1. The first two dissociation constants correspond to strong acids, and a single sharp break is obtained after the addition of two equivalents of alkali. A second break occurs after the addition of the third equivalent of alkali. As pk_4 corresponds to a very weak acid, no further break is obtained on further addition of alkali.

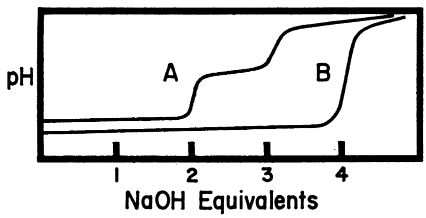
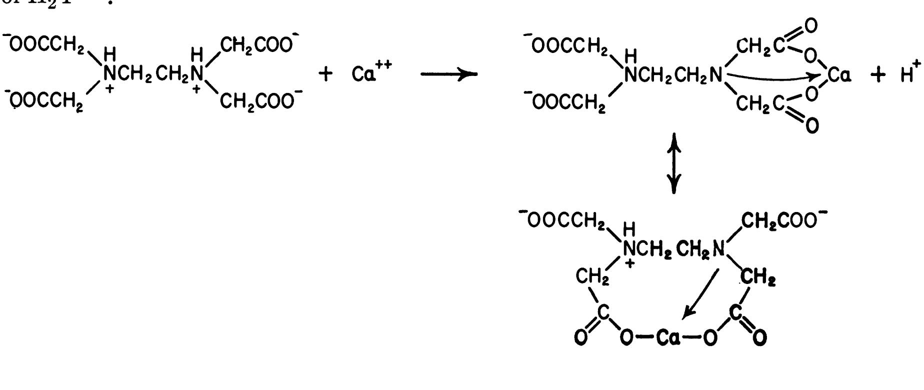


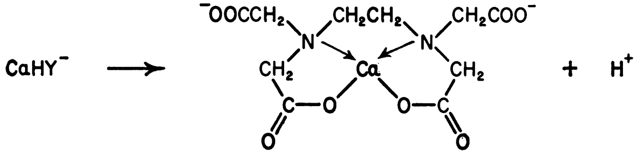
Figure 1. Titration of (ethylenedinitrilo) tetraacetic acid

A. No calcium ions present
B. Excess calcium ions present

In the presence of an excess of calcium ions, titration with alkali gives curve *B*, Figure 1: The presence of calcium ions causes all four protons to be dissociated readily, giving in effect a strong tetrabasic acid. The formation of the calcium chelate takes place according to the following reactions starting with the zwitterion form of H_2Y^{-2}:



The exact nature of $CaHY^{-}$ chelate is not known, but it is shown in the two most likely forms. As more alkali is added, the calcium coordinates with both nitrogens forming CaY^{-2} and releasing another proton:



CaY^{-2}

The successive displacement of the two nitrogen-bound protons is summarized in the following equations:

$$Ca^{+2} + H_2Y^{-2} \rightleftharpoons CaHY^{-} + H^{+}$$
$$Ca^{+2} + HY^{-3} \rightleftharpoons CaHY^{-}$$
$$CaHY^{-} \rightleftharpoons CaY^{-2} + H^{+}$$

The shape of curve *B*, with only one break at four equivalents of alkali, shows that all four protons are titrated together. Thus, in the presence of calcium ions, the four acid groups of EDTA have about equal acidity and the intermediate $CaHY^{-}$ has only a transient existence when alkali is continuously added. The stability constant for CaY^{-2} is defined by *K*.

$$Ca^{+2} + Y^{-4} \rightleftharpoons CaY^{-2} \qquad K = \frac{[CaY^{-2}]}{[Ca^{+2}][Y^{-4}]}$$

Stability Constants

The stability constants of a large number of metal chelates of EDTA have been determined. The pK's (log *K*) for some of the commoner metals are given in Table I (*6, 7*).

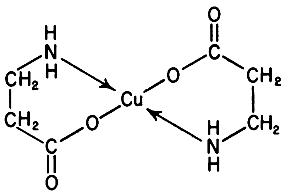
Table I. Stability Constants of Metal Chelate of EDTA

Ion	pK	Ion	pK
Li^{+}	2.79	Mn^{++}	13.47
Na^{+}	1.66	Co^{++}	16.10
Mg^{++}	8.69	Cu^{++}	18.38
Ca^{++}	10.59	Ni^{++}	18.54
Sr^{++}	8.63	Cd^{++}	16.48
Ba^{++}	7.76	Pb^{++}	18.20
Zn^{++}	16.58	La^{+++}	15.4
Fe^{++}	14.22	Fe^{+++}	25
		Cr^{+++}	24

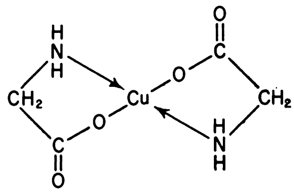
For a given chelating agent, the bond strength between metal and ligand may vary widely (Table I). Properties of the metals such as atomic number, valence, ionization potential, ionic radius, and *d*-orbitals all contribute to chelate stability. The univalent metals form very weak chelates and the multivalent metals form the stronger chelates. The order of stability of chelates of various metals is approximately the same for a large number of chelating agents. The order of chelate stability for EDTA and the alkaline earth series is barium < strontium < magnesium < calcium. Magnesium occupies a variable position; with some chelating agents it forms more stable complexes than calcium, although for the polyaminocarboxylic acids the calcium chelate is more stable. The stabilities of some of the bivalent transition metals with chelating agents generally follow the following order: manganese < iron < cobalt < nickel < copper > zinc.

For a given metal, the structure of the chelating agent is important in determining the chelate stability, the two most important factors being the number of atoms

in the chelate ring and the number of chelate rings formed. In general only five- or six-membered rings are encountered. The five-membered ring is favored and more stable when the ring is completely saturated, whereas the six-membered ring is favored if one or two double bonds are present. The experimental values of the stability constants of the 1 to 2 chelates formed between cupric ion and glycine and β-alanine illustrate the effect of ring size on chelate stability. Glycine, which forms five-membered chelate rings, has a pK value of 15.6 (*9*); β-alanine, which forms six-membered chelate rings, has a pK value of 12.8 (*8*).



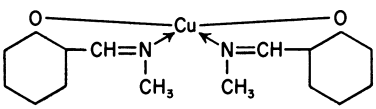
Cupric bis(β-alaninate)



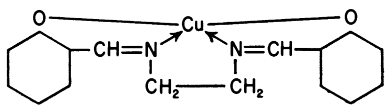
Cupric bis(glycinate)

Because pK's are log values, the glycine chelate is almost 1000 times as stable as the β-alanine chelate.

An increase in number of rings within a particular chelate structure increases the chelate stability. Calvin and Bailes (*3*) studied the copper chelates of the salicylaldimines of methylamine and ethylenediamine. The two structures are very similar, except that the ethylenediamine derivative has one additional chelate ring.

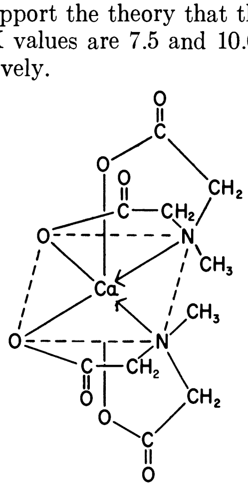


Cupric bis(salicylidinemethylamine)

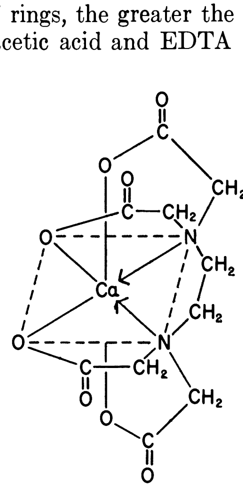


Cupric *N,N'*-disalicylidineethylenediamine

The half-wave potentials of the two copper chelates, determined using a dropping mercury electrode, were +0.02 and −0.75. As a greater negative value indicates a more stable chelate, the additional chelate ring present in the ethylenediamine derivative seems to increase the stability. Another set of chelates which illustrates this principle is the calcium chelates of *N*-methyliminodiacetic acid and EDTA. These two chelates, which differ only in that the EDTA chelate has one additional chelate ring, support the theory that the greater the number of rings, the greater the stability. The pK values are 7.5 and 10.6 for the methyliminodiacetic acid and EDTA (*11, 12*), respectively.



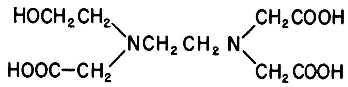
Calcium bis(*N*-methyliminodiacetate)

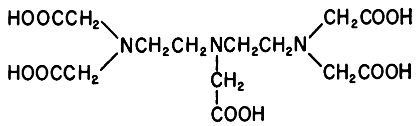


Calcium (ethylenedinitrilo)tetraacetate

Commercial Importance

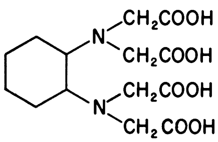
A promising use for metal chelates is the treatment of metal-deficient plants. Iron deficiency in plants inhibits chlorophyll synthesis. The leaves become light green or yellow; if not corrected, the result is stunted growth, reduced yields, and ultimately death of the plant. Stewart and Leonard (*13*) showed that severe cases of iron chlorosis could be corrected quickly and dramatically by applying small quantities of the iron chelate of EDTA. Iron EDTA was effective only on acid soils and other chelating agents were developed for more alkaline soils. The iron chelates of hydroxyethylethylenediaminetriacetic acid (HEEDTA) and diethylenetriaminepentaacetic acid (DTPA) have reached commercial importance also.

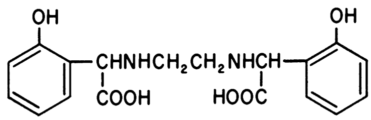




Hydroxyethylethylenediaminetriacetic acid **Diethylenetriaminepentaacetic acid**

It is estimated that 1,000,000 to 1,500,000 pounds of these metal chelates were sold in 1956. Both cyclohexanediaminetetraacetic acid (CDTA) and Chel 138, an





Cyclohexanediaminetetraacetic acid **Chel 138**

aromatic aminopolycarboxylic acid, have proved more effective on alkaline soils than any of the iron chelates commercially available. These chelates, however, have been produced only on a pilot plant scale. The iron chelate of Chel 138 has created interest among government and university experimenters for use on the calcareous soils of the South, Southwest, and Far West. It is effective in small quantities even on extremely alkaline soils and relatively nontoxic even in large doses. To date this chelate has not been produced in quantity because of the high production costs, but efforts are being made to overcome this obstacle.

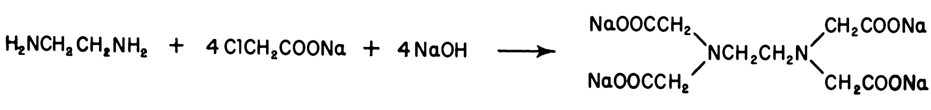
Other metal deficiencies in plants have been treated successfully with metal chelates of EDTA and diethylenetriaminepentaacetic acid. Chelates of zinc, copper, and manganese have been used on a limited scale.

In addition to its agricultural use, sodium ferric EDTA has found use in the synthetic rubber industry. As a component of the polymerization catalyst, it results in a more uniform product than could be previously obtained. The exact mechanism is not known, but the metal chelate may be involved in an oxidation-reduction system which regulates the rate of polymerization.

The calcium chelate of EDTA (Na_2CaY) has found some use as a pharmaceutical for treating lead and other heavy metal poisoning. Its use for the rapid removal of radioactive metals from the body is also indicated. The heavy metals form chelates with EDTA which are more stable than the calcium-EDTA chelate and hence will replace calcium; the heavy metal chelate is excreted in the urine. The quantity of chelate sold for this purpose is very small compared with other uses.

Four general methods have been used to prepare EDTA and related compounds.

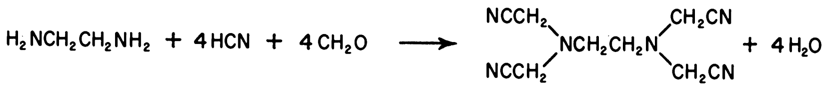
1. Chloroacetic acid will react with ethylenediamine under alkaline conditions (*10*):

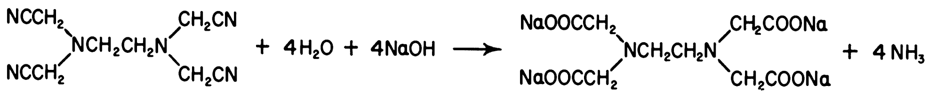


Good yields of the tetrasodium salt can be obtained by the proper control of conditions, and the free acid is precipitated by acidification with mineral acids. Solutions of the tetrasodium salt can be converted to the iron chelate as follows:

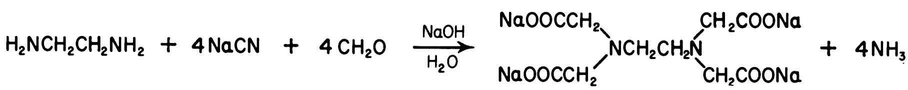
$$Na_4Y + FeCl_3 \longrightarrow NaFeY\downarrow + 3\,NaCl$$

2. In the method developed by I. G. Farbenindustrie A. G. (*2*) ethylenediamine, formaldehyde, and hydrogen cyanide (formed in solution by the reaction of sodium cyanide with acid) react. The process requires the isolation of the intermediate (ethylenedinitrilo)tetraacetonitrile, but the added step ensures that the tetrasodium EDTA formed by hydrolysis of the nitrile is not contaminated with impurities or inert salts.

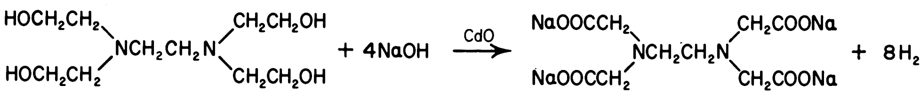




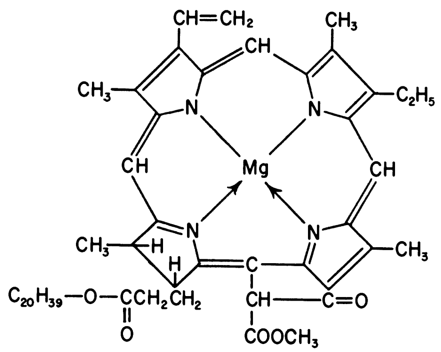
3. The process developed by Bersworth (*1*) converts ethylenediamine to the tetrasodium salt of EDTA by the simultaneous addition of sodium cyanide and formaldehyde to a sodium hydroxide solution of the diamine. The success of this process depends on the complete removal of the ammonia as it is liberated in the reaction. For this reason, EDTA made by this process always contains some nitrilotriacetic acid.



4. A catalytic oxidation of tetra (hydroxyethyl)ethylenediamine to EDTA has been developed (*5*). The amino alcohol is heated with sodium or potassium hydroxide and a cadmium oxide catalyst at 220° to 230°C. for several hours. Hydrogen is liberated and the tetrasodium salt of EDTA is obtained in about 85% yield. This method, however, has not attained the commercial importance of the other methods.

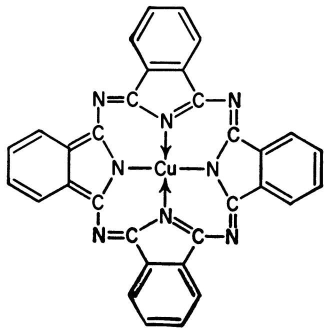


Metal chelates are not new. The naturally occurring metal porphyrins have been known for many years. The best known members of this class of compounds are heme, an iron-containing chelate present in animal blood, and chlorophyll, a magnesium-containing chelate present in all plants. All of the porphyrin structures are similar, in that they consist of four pyrrole nuclei joined at their alpha carbon atoms by methene groups. Chlorophyll a is the most prevalent form.



Chlorophyll a

The metal porphyrins are extremely stable chelates. In most cases it is impossible to remove the metal atom without destroying the rest of the molecule. Although chlorophyll, because of its antibacterial properties, created interest as a deodorant, its annual production is rather small. For the last few years the production of chlorophyll in this country has remained at about 12,000 to 15,000 pounds per year, whereas in the peak year of 1952 it reached about 100,000 pounds. A class of synthetic chelates which are structurally related to the porphyrins is being produced in appreciable quantities. These compounds are known as the metal phthalocyanines and are used as dyes and pigments. The structure of copper phthalocyanine is:

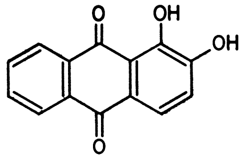


It was discovered in 1927 and it was soon realized that the metal phthalocyanines offered promise as pigments. Considerable developmental work was carried out. Because they are extremely stable to light, acid, and alkali, they have been widely used as pigments for printing on paper and cloth and for the coloration of paper, rubber, plastics, linoleum, paints, and lacquers. The commercial phthalocyanine pigments range from blue to green. The 1956 United States production of phthalocyanine pigments was about 6,000,000 pounds.

To make the phthalocyanines useful as dyestuffs, it was necessary to substitute various groups in the molecule so that the resulting products would have application properties of direct, sulfur, or vat dyes. For direct dyes, solubilizing groups such as sulfonic acid, carboxyl, and quaternary groups have been used. There are two ways of preparing these phthalocyanine derivatives: The phthalocyanine pigment can be made first and then the substituent added, or the phthalocyanine precursor can be substituted and then converted to the phthalocyanine. The 1956 production of phthalocyanine dyes was only about 763,000 pounds. Commercially, the phthalocyanines are prepared by heating a phthalic acid derivative mixed with a metal salt, urea, catalyst, and a high boiling inert solvent to a temperature of about 200°C. Yields of 85 to 98% of theory can be obtained.

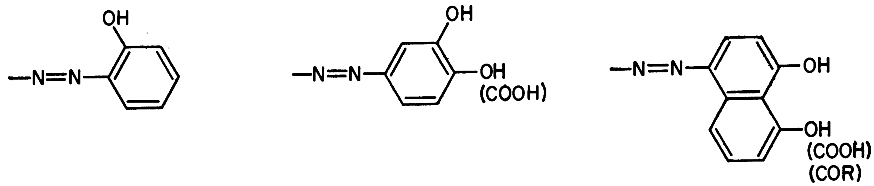
The phthalocyanines represent only one class of metal chelates which are useful as dyes and pigments. Actually, chelation can occur with any class of dyes which has the necessary donor groups in the proper positions. Examples are compounds having hydroxyl, carboxyl, keto, oximino, and amino groups in either ortho or peri position with respect to each other, or one of the above groups in the ortho position with respect to an azo (—N=N—) or an azomethine (—N=C<) linkage. The chelate can be formed on the fabric, as in mordant, chrome, and aftertreated direct dyes; or the chelate can be formed prior to application as in premetallized acid and coppered direct dyes.

Many of the first dyestuffs used by man were naturally occurring chelating agents which were converted to metal chelates on the fabric during the dyeing operation. Madder, a dyestuff known to the ancient Egyptians, was used with various metals such as chromium, aluminum, iron, copper, and tin in the mordant dyeing of cotton. Alizarin, the principal coloring matter in madder, was discovered in 1824.



Alizarin

In 1869, it was first prepared synthetically from anthraquinone. By 1871 the process was developed sufficiently so that synthetic alizarin could compete with the natural product, and soon the natural product was supplanted by the synthetic material. Many alizarin derivatives have been prepared and found useful as mordant dyestuffs, used principally for dyeing cotton. Alizarin has been used to some extent for wool dyeing also, but this is accomplished better by the so-called chrome dyes. These are generally azo dyes containing the following groupings:



The mordanting metal is generally chromium, although aluminum and iron are also used. In 1956, mordant and chrome dyes represented a market of about $6,500,000 in the United States.

In the last 15 to 20 years, a new group of dyes have joined the class of metal chelates formed on the fabric. These are the aftertreated direct dyes for cotton, which are dyed onto the fabric and then aftertreated with copper salts. The chelate is formed on the fabric giving a very light- and washfast color. Many of the aftertreated direct dyes have been premetallized with copper and are useful as lightfast, direct cotton dyes, thus simplifying the dyeing process.

Probably the fastest growing class of chelate dyes are the premetallized dyes for wool and nylon. These dyes are generally azo compounds having hydroxyl, amino, or carboxyl groups ortho to the azo grouping. The chelate is formed in manufacture, and the dyes are sold as the metal chelates.

The first dyes to appear in this class were the 1 to 1 dye-chromium chelates, which contained sulfonic acid groups for increased solubility. These are used for dyeing wool and are analogous to the chrome dyes, except that the chelate is formed before application. However, they are less washfast than the chrome dyes.

More recently a class of premetallized dyes containing a dye to metal ratio of 2 to 1 has been developed. These dyes are usually cobalt or chromium chelates, containing no sulfonic acid groups but having sufficient solubility or dispersibility for practical application. They are wash- and lightfast and have the added feature of level and penetrating dyeing from a neutral dye bath, whereas the chrome dyes and the 1 to 1 premetallized chelates must be applied from a strongly acid bath.

A new class of premetallized dyes developed by the Geigy Chemical Corp. are 2 to 1 cobalt or chromium chelates. These are soluble in acetone and alcohol and have created interest in the mass dyeing of acetate rayon, replacing pigments. It is estimated that premetallized dyes had a sales volume in the United States of about $2,000,000 in 1956. This was expected to increase considerably during the next few years.

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Manufacture, Properties, and Uses of Organolithium Compounds

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The various methods of preparing organolithium compounds and the effect on such preparations of factors such as particle size of the lithium metal, solvent, temperature, and time are reviewed. Particular emphasis is placed on some recent studies which show that lithium dispersions can be used to advantage in the preparation of organolithium compounds. For example, phenyllithium can be prepared from chlorobenzene satisfactorily by using lithium dispersions. The general physical and chemical properties of organolithium compounds of interest to commercial producers and users are covered. Comparisons of stabilities of various types of organolithium compounds are of particular interest. In general, only the aryllithium compounds are sufficiently stable in ether to allow extended storage. Even in hydrocarbon solvents, such as benzene and petroleum ether, storage of organolithium compounds at temperatures of 0°C., or lower, is recommended. A review is presented of the more important present and potential commercial uses of organolithium compounds.

Organolithium compounds have received attention as reagents for commercial use only in recent years. This is undoubtedly a reflection of the increasing amount of research that is being carried out each year on these compounds. The fact that more papers were published on organolithium chemistry in the 2-year period, 1954-1955, than had appeared altogether prior to 1949, underlines the tremendous increase in interest in this field of chemistry.

Despite this increased concentration of research effort, a review of the literature on organolithium chemistry reveals that interest is still chiefly centered on the uses of these compounds. For example, although well over one hundred organolithium compounds are reported in the literature as having been prepared in solution, scarcely a dozen have been isolated as pure compounds. Even those that have been isolated have been examined only superficially. Not only is information of a fundamental nature almost nonexistent, but knowledge of a practical type is also very limited. In only a few isolated instances have systematic studies been carried out on the effect of variations in solvent, temperature, and time on the yields obtained in organolithium preparations. Optimum conditions for carrying out reactions involving organolithium

compounds have been determined in even fewer cases. At present, therefore, consideration of the possible use of an organolithium compound in a commercial process almost invariably involves carrying out a more or less extensive program of research to determine optimum conditions for preparing and using the compound. In this paper the author has attempted to assemble as much as possible of the most important information on the preparation, properties, and uses of organolithium compounds. He has tried to stress the areas deemed of greatest importance to those interested in commercial uses of these compounds, and to indicate areas where research is urgently needed.

Preparation of Organolithium Compounds

The preparations of organolithium compounds can be divided into two major groups: those which use metallic lithium and those which use another organolithium compound as the source of the lithium atom. In the following listing of the main procedures which have been used, the first four methods use metallic lithium and the others use an organolithium compound. Only one or two typical examples have been given in each case.

Organolithium compounds have been prepared by:

1. Direct addition of lithium metal to a carbon-carbon unsaturated bond (*52*):

$$C_6H_5CH{=}CHC_6H_5 + 2Li \rightarrow C_6H_5CH(Li)CH(Li)C_6H_5$$

2. Metal-metal exchange (*22, 51, 53, 55*):

$$R_2Hg + 2Li \rightarrow 2RLi + Hg$$

$$RMgCl + 2Li \rightarrow RLi + LiCl + Mg$$

3. Hydrogen-metal exchange (*7*):

$$RC{\equiv}CH + 2Li \xrightarrow[NH_3(1)]{} RC{\equiv}CLi\ (+LiH)$$

4. Halogen-metal exchange (*7, 13, 67*):

$$RX + 2Li \rightarrow RLi + LiX$$

5. Addition of an organolithium compound to a carbon-carbon unsaturated bond (*51, 54, 64, 65*):

$$>C{=}C< + RLi \rightarrow >C(R){-}C(Li)<$$

6. Hydrogen-metal interconversion (metalation) (*29*):

$$RH + R'Li \rightarrow RLi + R'H$$

7. Metal-metal interconversion (*55, 68*):

$$R_2Hg + 2R'Li \rightarrow 2RLi + R'_2Hg$$

$$C_6H_5CH_2MgCl + 2C_6H_5Li \rightarrow C_6H_5CH_2Li + (C_6H_5)_2Mg + LiCl$$

8. Halogen-metal interconversion (*41*):

$$RX + R'Li \rightarrow RLi + R'X$$

9. Disproportionation (*66*):

$$2LiCH_3 \xrightarrow[200\text{–}240^\circ C.]{} Li_2CH_2 + CH_4$$

Only the first four methods involve direct preparation of an organolithium compound. Methods 5, 6, 7, and 8 depend upon the use of an organolithium compound prepared by one of the first four methods. Thus, while the last four methods, and particularly Method 8, are useful for the preparation of numerous organolithium com-

pounds, principally on a laboratory scale, commercial usefulness depends primarily upon the feasibility of preparing the intermediate organolithium compound. Consequently, the author discusses mainly Methods 1, 2, 3, and 4.

The direct addition of lithium metal to an unsaturated linkage (Method 1) occurs in only a few special cases. This severely limits any use of this method, particularly on a commercial scale.

The metal-metal exchange procedure of Method 2 was important during the early investigations on organolithium compounds but is largely only of historical interest now. More convenient preparatory methods are now available, except in a few special cases—e.g., the preparation of benzyllithium via benzylmagnesium chloride. The use of the hydrogen-metal exchange reaction (Method 3) has to date been limited to the preparation of a few alkynyllithium compounds. At present there is no published account of the use of this procedure for the preparation of an alkyl or aryllithium compound.

The metal-halogen exchange reaction of Method 4 is today the procedure used almost exclusively in the preparation of organolithium compounds from lithium metal. It can be carried out conveniently and rapidly in relatively simple equipment to give high yields of the desired organolithium product. A number of reviews (*7, 9, 13, 29, 41, 43, 45, 56, 61*) of organolithium chemistry contain either detailed instructions or references to sources of experimental details for the preparation of specific organolithium compounds. Consequently, no detailed coverage is given here. In general, yields of primary organolithium compounds of 75 to 90% are readily obtainable under the proper conditions.

The process of Method 4 suffers from the fact that an organic halide, and often containing a particular halogen, is a necessary starting material. While such compounds are usually obtainable in adequate supply, the price is often such as to discourage large-scale usage, particularly when it is necessary to use an organic bromide. In general, the bromides of lower molecular weight cost about twice as much as the chlorides, yet in some instances—e.g., the preparation of phenyllithium—convenience in handling, higher yields, cleaner products, etc., make the bromide the reagent of choice.

Preparations of organolithium compounds can be made in various ethers (dialkyl ethers, dioxane, tetrahydrofuran, etc.), hydrocarbon solvents (benzene, cyclohexane, petroleum ether, etc.), and liquid ammonia in the special case of alkynyllithium compounds. Reagents and solvents should be as pure as possible, and should be thoroughly dry. A blanket of inert gas (nitrogen, helium, or argon) should be maintained over the reaction mixture at all times. The temperature at which the preparation is carried out may vary from $-75°$ to the boiling point of the solvent, depending upon the particular substance desired. Similarly, the time required for carrying out the preparation will vary from a few minutes to several hours.

Yields of alkyllithium compounds are best determined by the method of double titration (*19*). In this procedure one sample of the solution of organolithium compound is hydrolyzed directly while a second sample is treated with benzyl chloride prior to titration with standard acid. Calculations based on the difference in the two titrations give a more accurate yield determination than does the older procedure of simply titrating the sample that is hydrolyzed directly.

The solvent used in carrying out the organolithium preparation exerts a definite effect on the yield obtained and the time required for the reaction to go to completion. In general, ethers accelerate the reaction while hydrocarbon solvents tend to retard the reaction. For example, when the preparation of 1-naphthyllithium by the reaction of 1-bromonaphthalene with alkyllithium compounds was carried out in various solvents (*28*), the rate of the reaction depended upon the solvent used. The effectiveness of the solvents was found to decrease in the following order:

$$(C_4H_9)_2O > (C_2H_5)_2O > C_6H_5N(CH_3)_2 > C_6H_6 > \text{cyclohexane} > \text{petroleum ether}$$

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In some cases a change in the solvent has been found even to change the course of the reaction. For example, this effect was observed in the reaction of *n*-butyllithium with β-bromostyrene (*27*). With low boiling petroleum ether as the solvent, the product was found to be β-styryllithium, whereas when diethyl ether was used, phenylethynyllithium was obtained:

$$C_6H_5{-}CH{=}CHBr + n\text{-}C_4H_9Li \xrightarrow{(C_2H_5)_2O} C_6H_5{-}C{\equiv}CLi$$

$$C_6H_5{-}CH{=}CHBr + n\text{-}C_4H_9Li \xrightarrow{\text{Pet. ether}} C_6H_5{-}CH{=}CH(Li)$$

In preparing organolithium compounds from lithium and organic halides, the halide atom present has been found to affect the rate and extent of reaction markedly. Experience has shown that two of the most commonly used organolithium compounds, *n*-butyllithium and phenyllithium, can best be prepared from the respective bromides. Organic bromides, in general, however, cost about twice as much as the corresponding chlorides. It would, therefore, be beneficial from a commercial standpoint if organic chlorides could be used.

It was observed over 25 years ago by Gilman and coworkers (*36*) that the smaller the pieces of lithium could be made the higher the yield and the shorter the time required for the organolithium preparation to be completed. For many years the particle size was determined by the patience of the researcher in cutting the metal with scissors, knives, paper cutters, etc. His task was considerably eased about 10 years ago with the advent of lithium wire and ribbon.

Gilman and coworkers (*36*) also observed that the next significant advance in making organolithium compounds more accessible would probably come with a convenient procedure for the preparation of lithium dust or granules. The description about 9 years ago by Perrine and Rapoport (*49*) of a procedure for the preparation of lithium sand was a step in this direction. The use of lithium sand reportedly gave increased yields of organolithium compounds and within a short time lithium sand could be, and still can be, purchased on a commercial basis.

The latest advance in producing lithium metal in small particle size has come within the past 2 years with the development of lithium dispersions to a point where they can now be purchased on a small lot basis. To date these dispersions have been offered only in paraffin hydrocarbon mediums—i.e., mineral oil, petrolatum, and wax—although conceivably other mediums could be easily used.

Up to now, no complete report of studies on the use of lithium dispersions in the preparation of organolithium compounds has appeared. Some work has been done, however, as evidenced by the reference by Gilman and Gorsich (*18*) in 1955 to unpublished studies by K. Oita. They reported that improved yields of some organolithium compounds were obtained when lithium dispersions were used. Also, in 1956, Hart and Sandri (*38*) reported the first successful preparation of cyclopropyllithium from cyclopropyl chloride through the use of finely powdered lithium.

To confirm this statement, the author has carried out a limited research program on the use of lithium dispersions in the preparation of organolithium compounds. As a starting point he chose the preparation of phenyllithium from chlorobenzene, because failure to obtain good yields from the reaction of chlorobenzene with bulk lithium in the past has necessitated the use of the more expensive bromobenzene. The results of some of the runs are given in Table I.

The preparations were carried out in the usual apparatus consisting of a four-necked flask equipped with a Tru-bore stirrer, thermometer, reflux condenser, and dropping funnel arranged so that a blanket of inert gas could be maintained over the reaction mixture.

The data in Table I show that under comparable conditions, appreciably higher yields of phenyllithium are obtained with lithium dispersions than with lithium wire.

Table I. Phenyllithium Preparation from Chlorobenzene

Expt. No.	Inert Gas[a]	Li Form	Li, G. At.	PhCl,[b] Mole	Ether, Ml. In flask	Ether, Ml. In funnel	Temp.,[c] °C.	Time Addn. PhCl Soln., Min.	Time after Addn., Hr.	Yield PhLi by Titn., Wt. %	PhCl Recovd., Wt. %	Benzoic Acid Yield, Wt. %
1	N_2	Wire[d]	1.1	0.5	100	150	39	100	4	5	80	5[e]
2	A	Wire	1.1	0.5	150	100	38	50	4.3	5	72	8[f,g]
3	N_2	Dispn.[h]	1.1	0.5	150	100	39	40	1.3	—	69	12[e,i]
4	A	Dispn.[h]	1.1	0.5	150	100	38	50	4.2	—	56	23[e,i]
5	A	Wire	1.1	0.5	150	100	−10 to −20	35	4.8	65	22	71[f,k]
6	A	Dispn.[l]	1.1	0.5	150	100	−15 to −30	35	4	100[m]	5	93[f]

[a] Commercial product used without further purification.
[b] Fisher Certified chlorobenzene in ether solution in dropping funnel.
[c] Reaction was started by adding 5 to 10 ml. of chlorobenzene solution, then brought to reaction temperature.
[d] Wiped free of grease, then rinsed in ether.
[e] Phenyllithium was carbonated by pouring onto dry ice–ether slurry and benzoic acid recovered by extracting ether layer with dilute NaOH followed by acidification of combined alkaline layers.
[f] Same as *e*, but carbonated mixture acidified, extracted with ether, and benzoic acid isolated by distillation of dried ether layer.
[g] About 5 grams of mixture of amber liquid and solid with a strong ketone odor.
[h] Caked material which had settled out from dispersion in mineral oil; particle size < 40 microns in diameter.
[i] In addition, appreciable amounts of ketonic material formed.
[k] A 31% yield of benzoic acid and a 40% yield of benzophenone.
[l] About 25 grams of dispersion containing 30 wt. % of lithium, 63 wt. % of mineral oil, and 7 wt. % of petrolatum; particles < 25 microns in diameter.
[m] High yield due to inclusion in sample of unreacted lithium metal.

In the runs carried out with lithium wire at room temperature, the metal rapidly became coated with a dark solid. It seemed most logical that the coating was diphenyl formed by reaction at the metal surface of chlorobenzene and phenyllithium. If this were true, it seemed reasonable that diphenyl formation would be suppressed by lowering the temperature. As shown in Experiment 5, a much higher yield of phenyllithium was obtained at the lower temperature and the lithium metal became coated only very slowly. This, of course, does not prove that suppression of diphenyl formation gave the increased yield, although such a conclusion appears logical.

The results of experiment 6, Table I, show that by using dispersed lithium and temperatures below −10°, phenyllithium can be prepared from chlorobenzene in yields over 90%. Additional work may show that conditions can be adjusted so that chlorobenzene, rather than bromobenzene, can be used in the commercial preparation of phenyllithium and thereby reduce the cost appreciably.

Physical Properties of Organolithium Compounds

The determination of the physical properties of pure organolithium compounds is an area of research where very little has been done and much needs to be done.

The alkyllithium compounds are colorless liquids, except the methyl and ethyl derivatives, which are white solids at room temperature. Phenyllithium is also a white solid. Benzyllithium and triphenylmethyllithium are presumably colored yellow, as their solutions are yellow.

All of the pure organolithium compounds that have been examined have been found to burn vigorously in air. Even when the substances are in solution, care must be exercised in keeping them away from contact with the air. Otherwise, the reaction with air evolves so much heat that the solvent may be ignited.

Organolithium compounds, in general, are more stable thermally than similar compounds of the other alkali metals. This, however, is only a matter of degree, as propyllithium and butyllithium have been shown to decompose at elevated temperatures to yield lithium hydride and the corresponding olefin (*70*):

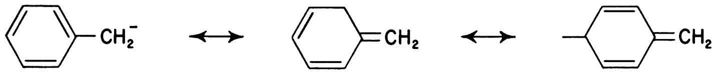
$$R{-}CH_2{-}CH_2Li \xrightarrow[\Delta]{} R{-}CH{=}CH_2 + LiH$$

While this thermal decomposition is slow at room temperature, solutions of alkyllithium compounds in inert solvents, such as petroleum ether, are known to decrease in strength on long standing. Aryllithium compounds, however, are apparently much more stable to heat than alkyllithium compounds, although here, again, fundamental data are missing. The thermal stability of organolithium compounds becomes of importance in considering the manufacture and storage of such materials for commercial use. No thorough study of this problem has been reported as yet.

In general, organolithium compounds are readily soluble in ethers such as diethyl ether and tetrahydrofuran, and, to a lesser degree, in hydrocarbons such as benzene, cyclohexane, and petroleum ether. As a rule ethers accelerate the preparation and reactions of organolithium compounds, whereas hydrocarbons have a retarding effect. This increased activity in ethers, however, is also evidenced toward the solvent itself, so that cleavage of the ether is relatively rapid, particularly with alkyllithium compounds (*19, 63*). For example, whereas an ether solution originally $0.4M$ in phenyllithium required about 12 days to fall to $0.2M$ when kept at 35°, the concentration of *n*-butyllithium in an ether solution kept at 25° dropped to half its original strength in about 7 days (*19*). However, ether solutions of *n*-butyllithium apparently can be kept for 4 days or longer without significant decomposition if the temperature is maintained at or below 10° (*14*). This indicates that for prolonged storage of organolithium compounds, temperatures of about 0° should be used. In contrast to this, a benzene solution of ethyllithium was reported to be unchanged after standing 2 months (*25*).

Chemical Properties of Organolithium Compounds

Alkyllithium compounds are considered to be predominantly covalent, rather than saltlike, materials, as evidenced by the nonconductance of solutions of ethyllithium in benzene (*39*) and by the low dipole moment (0.97 D) of *n*-butyllithium which indicates about 40% ionic character for the carbon-lithium bond (*50*). Ionic character increases, however, in going from simple alkyl compounds to substances such as benzyllithium and triphenylmethyllithium due to anion stabilization through resonance:



A number of different studies have established that organolithium compounds are intermediate in activity between the Grignard reagents and the organometallic compounds of the other alkali metals. For example, the reaction of phenylmetallic compounds with azobenzene gave the following decreasing order of activity (*15*):

$$\text{PhK} > \text{PhCaI} > \text{PhNa} > \text{PhLi} > \text{PhMgBr} > \text{Ph}_2\text{Be} > \text{PhMnI} > \text{Ph}_2\text{Zn}$$

In another study (*35*), the decreasing order of reactivity of the phenylethynyl derivatives towards benzonitrile was shown to be:

$$\text{RCs} > \text{RRb} > \text{RK} > \text{RNa} > \text{RLi} > \text{RMgBr}$$

The relative reactivity of an organolithium compound also varies greatly with respect to the hydrocarbon radical present. In the halogen-metal interconversion reaction of 1-bromonaphthalene with various organolithium compounds, the following decreasing order of activity was observed (*28*):

$$n\text{-C}_3\text{H}_7 > \text{C}_2\text{H}_5 > n\text{-C}_4\text{H}_9 > \text{C}_6\text{H}_5 > \text{CH}_3$$

In the metalation of dibenzofuran in ether (*29*), the following slightly different order of decreasing activity was obtained:

$$n\text{-C}_4\text{H}_9 > \text{C}_2\text{H}_5 > n\text{-C}_5\text{H}_{11} > \text{C}_6\text{H}_5 > \text{CH}_3$$

Recently it has been shown (*3*) that the decreasing order of activity of branched-chain alkyllithium compounds towards addition to ethylenic double bonds is:

$$\text{R}_3\text{C} > \text{R}_2\text{CH} > \text{RCH}_2$$

The above examples show that there is a wide variation in the reactivity of organolithium compounds which depends only on the structure of the compound. When considering the possible use of an organolithium compound, this variation in reactivity with structure must be considered along with the effects of solvent, time, and temperature.

Uses of Organolithium Compounds

The only reported instance of the use of organolithium compounds as such is the use of alkyllithium compounds as catalysts for the polymerization of olefins (*1, 10, 12, 37*). In all other cases, the organolithium compound has been used as an intermediate in the preparation of some other desired material. Consequently, a discussion of the uses of organolithium compounds is primarily a discussion of the reactions of organolithium compounds.

For the purposes of this paper, the reactions of organolithium compounds have been divided broadly into two main types: substitution (interconversion) reactions and addition reactions. Only a brief mention is made of those few instances in which organolithium compounds undergo reactions of other types, such as elimination reactions and molecular rearrangements.

Substitution Reactions of Organolithium Compounds

Hydrogen-Metal Interconversion (Metalation) Reactions. This is the same type of reaction as that given for preparation Method 6, and is called a metalation reaction. An interesting variation of this reaction is that used to prepare lithium compounds such as triphenylgermyllithium (*17*):

$$(C_6H_5)_3GeH + RLi \rightarrow RH + (C_6H_5)_3GeLi$$

As the metalation reaction with organolithium compounds has been covered in an excellent review by Gilman and Morton (*29*), only a brief discussion is given here.

The metalation reaction is used chiefly for the preparation of lithium derivatives which are difficultly obtainable otherwise. The reaction has been found suitable only when the compound to be metalated has present a hydrogen atom activated by an adjacent vinyl, aryl, alkoxyl, hetero, or similar group. This dependence upon an activated hydrogen atom limits the usefulness of the reaction to those compounds in which only one such atom is present. Otherwise, specificity of attack is lost and mixtures of products result.

Hydrogen-metal interconversion has been shown (*70*) to be the initial reaction involved in the cleavage of diethyl ether by *n*-butyllithium:

$$CH_3CH_2OC_2H_5 + n\text{-}C_4H_9Li \rightarrow CH_3CH(Li)OC_2H_5$$

$$CH_3CH(Li)OC_2H_5 \rightarrow CH_2{=}CH_2 + LiOC_2H_5$$

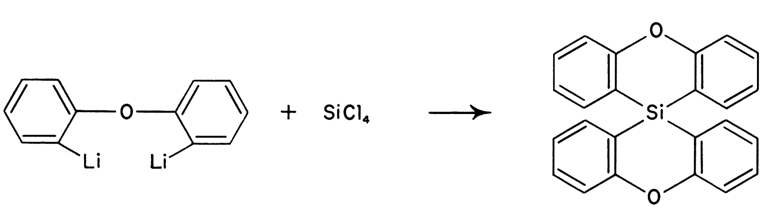
The hydrogenolysis of organolithium compounds (*20*) can be considered as a special case of hydrogen-metal interconversion:

$$RLi + H_2 \rightarrow RH + LiH$$

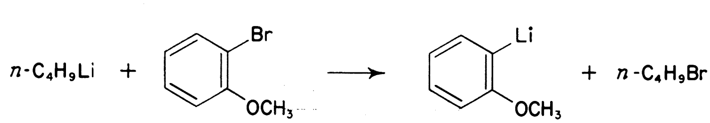
Metal-Metal Interconversion Reactions. The use of metal-metal interconversion reactions for the preparation of organolithium compounds was illustrated in Method 7. The chief use of organolithium compounds in such reactions, however, has been for the preparation of organic derivatives of other metals such as thallium (*4, 21, 23*), gold (*33*), germanium (*40*), silicon (*8, 11, 16, 34, 58*), tin (*2*), and lead (*2*) by the following general reaction:

$$MCl_x + xRLi \rightarrow R_xM + xLiCl$$

As a specific illustration, this procedure was recently used (*46*) for the preparation of some phenoxasilin derivatives, one of them being 10,10′-spirobiphenoxasilin:



Halogen-Metal Interconversion Reactions. The halogen-metal interconversion is illustrated by the following example (*26*):



This reaction finds its greatest use in the preparation of organolithium compounds which cannot be readily prepared by the direct action of lithium metal on the organic halide. A thorough discussion of the mechanism, scope, and experimental conditions

of this reaction has been given by Jones and Gilman (*41*). While the halogen-metal interconversion reaction has been used widely for experimental synthetic work, no extensive use on a commercial scale has been reported as yet.

Radical-Metal Interconversion Reactions. In this type of interconversion reaction the organolithium compound is destroyed as such in order to produce a desired end product.

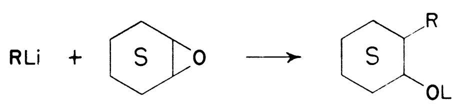
Hydrolysis is a simple example of this type of reaction:

$$RLi + HOH \rightarrow RH + LiOH$$

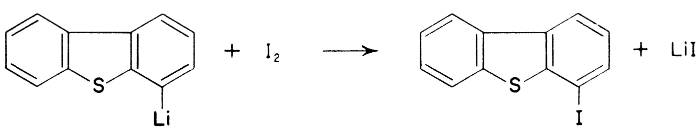
Alcohols, mercaptans, etc., enter into a similar reaction:

$$RLi + HOR' \rightarrow RH + LiOR'$$

The cleavage of epoxides and other cyclic ethers is a related reaction (*44*):



A special case of radical-metal interconversion is that involved in the preparation of organic halides by the reaction of organolithium compounds with halogens (*30*):



The formation of coupled products by the reaction of an organolithium compound with an organic halide is another case of radical-metal interconversion:

$$n\text{-}C_4H_9Li + n\text{-}C_4H_9X \rightarrow n\text{-}C_8H_{18} + LiX$$

Studies (*62, 67, 69*) of this coupling reaction have shown the iodine derivatives to be the most suitable, because, in general, they react most rapidly.

Addition Reactions of Organolithium Compounds

Addition to Inorganic Reagents. The formation of carboxylic acids by the reaction of organolithium compounds with carbon dioxide with subsequent hydrolysis has been widely used in laboratory studies on organolithium compounds:

$$RLi + CO_2 \longrightarrow RCO_2Li \xrightarrow{HOH} RCOOH$$

The reaction proceeds rapidly and to completion at low temperatures to form the carboxylic acids in good yields. When the carbonation is carried out at room temperature or higher, the chief products obtained are ketones (*5, 32, 42, 59*):

$$C_6H_5Li + CO_2 \longrightarrow C_6H_5COOLi \xrightarrow{C_6H_5Li} (C_6H_5)_2C{=}O + Li_2O$$

The preparation of hydroxy derivatives of organic compounds by the reaction of organolithium compounds with oxygen has been found to be satisfactory, particularly with aryllithium and heterocyclic lithium compounds (*47*):

$$C_6H_5Li \xrightarrow{O_2} C_6H_5OLi \xrightarrow{HOH} C_6H_5OH$$

Other similar addition reactions can be carried out as illustrated by the reaction of phenyllithium with nitrous oxide (*57*):

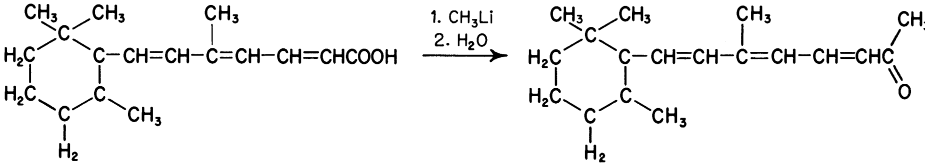
$$C_6H_5Li + N_2O \rightarrow C_6H_5N{=}NOLi \rightarrow C_6H_5H,\ C_6H_5{-}C_6H_5,\ C_6H_5N{=}NC_6H_5, \text{ etc.}$$

Addition to Carbon-Carbon Unsaturated Bonds. This type of addition reaction was illustrated in preparation Method 5. This is presumably the initial reaction involved in the catalytic polymerization of olefins by organolithium compounds (*37*). Although such catalytic uses have been reported to be only in the experimental stage, use on a commercial scale could conceivably develop.

Addition to Carbon-Oxygen Unsaturated Bonds. Probably the most useful reaction which organolithium compounds undergo is addition to carbon-oxygen unsaturated bonds. This is shown in the following typical reaction of a ketone with an organolithium compound to yield the lithium salt of a tertiary alcohol:

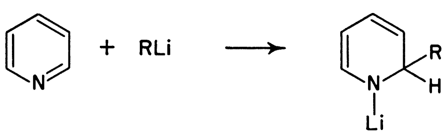
$$R_2C{=}O + R'Li \rightarrow R_2R'COLi$$

Similar reactions occur with aldehydes, carboxylic acids, esters, anhydrides, etc. This type of reaction has been used in the preparation of synthetic vitamin A (*60*) by the reaction of methyllithium with β-ionylidenecrotonic acid to yield on hydrolysis the desired ketone intermediate, I:

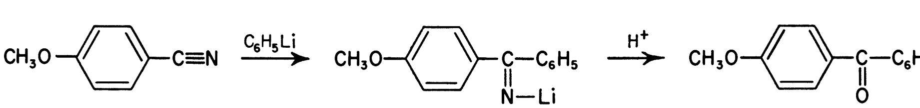


β-Ionylidenecrotonic acid I

Addition to Carbon-Nitrogen Unsaturated Bonds. Organolithium compounds have been found to add readily to carbon-nitrogen double and triple bonds. The following is an example of addition to a carbon-nitrogen double bond (*71, 72*):



Organolithium compounds add readily to carbon-nitrogen triple bonds as illustrated in the following reaction (*24*):

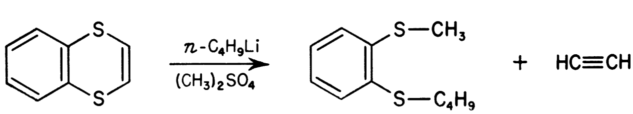


Although the reactions involving addition of organolithium compounds to carbon-nitrogen unsaturated bonds have beeen used widely for studies on a laboratory scale, no use on a commercial scale is known at present.

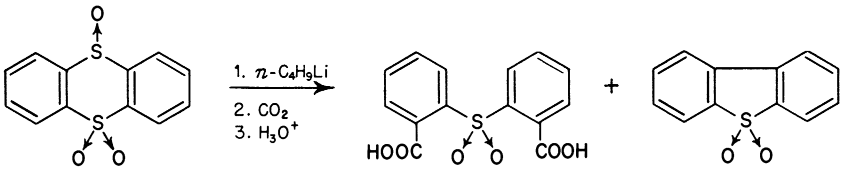
In the discussion of uses of organolithium compounds, only a very brief mention has been made of each of the major uses known. Many additional examples and detailed discussions can be found in general references (*3, 13, 21, 23, 29, 41, 43, 45, 56, 61*).

Miscellaneous Organolithium Reactions. Some recently reported uses of organolithium compounds illustrate further the wide range of possible reactions which these compounds can undergo.

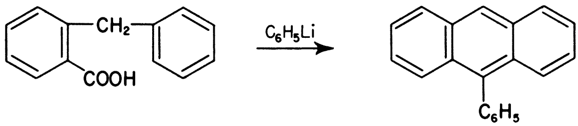
Of importance in synthetic work is the report (*48*) that butyllithium cleaves certain sulfide linkages with ease:



Certain sulfoxides also can be cleaved readily to yield interesting and useful products (*31*):



Phenyllithium has been found to catalyze cyclization reactions of the following types (*6*):



Use of this procedure for preparing 9-phenylanthracene derivatives is reportedly superior to other methods now known.

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Reduction of Organic Compounds by Lithium in Amines of Low Molecular Weight

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Lithium dissolved in amines of low molecular weight is a stronger reducing agent than sodium in ammonia. This reagent does not require addition of an acid such as alcohol to initiate the reaction. The mechanisms of the 1,4-reductions produced by the lithium-amine system are explained. Even at dry ice temperatures, compounds capable of conjugation are isomerized partially by the lithium alkylamides produced in the lithium-amine reductions. This is shown by inspection of the ultraviolet absorption spectra of the products.

The reduction of organic compounds by alkali or alkaline earth metals dissolved in liquid ammonia has been discussed extensively and is the subject of several excellent reviews (*5, 11, 12*).

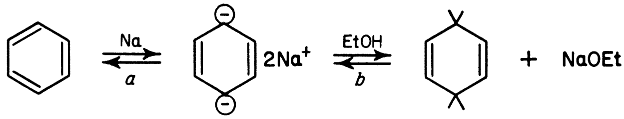
The ammonia brings relatively high concentrations of electrons and organic material into close proximity, permitting a smooth transfer of the electrons to the organic compound. The exact mechanism by which this electron transfer occurs has not been determined. The formation of an organometallic intermediate may be envisioned with relatively covalent carbon-metal bonds or simply electronic transfer, producing radical ions (one-electron transfer) or dianions (two-electron transfer), depending on the number of electrons captured initially by the organic material. These finer points of the mechanism are undetermined, but the gross features of the reductions can be expressed as a two-step process: electron transfer reversibly from the solvent or metal atoms to the organic compounds, and solvolysis of the resulting intermediate, with formation of a reduced product and an alkali or alkaline-earth amide. Thus, naphthalene is reduced by sodium in ammonia to Tetralin (*13*):



(1)

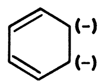
A variety of metals such as lithium, sodium, potassium, calcium, barium, and strontium have been used as reducing agents in conjunction with ammonia as the solvent. However, sodium in ammonia has been the most popular combination.

Often an acid such as methanol, ethanol, or ammonium chloride must be added to effect reduction in this system. Sodium in ammonia does not reduce benzene, toluene, xylene, and other aromatic compounds, but reduction of these materials will occur in the presence of alcohol (*12*) with the formation of 1,4-dihydro products.

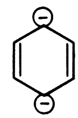


(2)

The 1,4-nature of these reductions can be rationalized by assuming a dianion intermediate. Energetically, a double negative charge would be more favorable in a 1,4- than in a 1,2-position. Thus, 1,4-reduction should proceed much more rapidly



Less stable



More stable

than a 1,2-reduction. Because reduction occurs only in the presence of ethanol, equilibrium *a* in Equation 2 should lie far to the left. The addition of ethanol, a stronger acid than ammonia, shifts this equilibrium to the right by protonating the dianion intermediate. Sodium ethoxide is formed concomitantly. The latter is not effective at −33° in causing an isomerization of the 1,4-dihydro product to a conjugated system. Hence, the reduction essentially stops at this point because of the slowness of 1,2-reductions.

Lithium dissolved in certain low molecular amines is a more powerful reducing medium than sodium in liquid ammonia (*1*, *3*, *4*). Isolated benzene rings are reduced selectively to mono-olefins by this reagent (*3*). Thus, benzene itself is reduced to cyclohexene (*3*), biphenyl to 1-cyclohexylcyclohexene (*3*), naphthalene to $\Delta^{9,10}$-octalin (1,2,3,4,5,6,7,8-octahydronaphthalene) (*3*), ethylbenzene to 1-ethylcyclohexene (*3*), and fluorene to 1,2,3,4-tetrahydrofluorene (*2*).

Aromatic compounds containing reducible functional groups are also attacked by the lithium-amine reagent. Acetophenone is reduced to α-Δ'-cyclohexenylethyl alcohol (*1*), 2-phenylethanol to β-Δ'-cyclohexenylethyl alcohol (*1*), and benzylnitrile to β-Δ'-cyclohexenylethylamine (*1*).

This reaction has been applied in steroid and ferrocene chemistry (*10*). In the latter instance, it holds promise for preparing substituted cyclopentadiene derivatives.

No acid substance such as alcohol needs to be added to the lithium-amine reagent to bring about reduction. A possible explanation is that equilibrium *a* in Equation 2 lies farther to the right in the lithium-amine system. Undoubtedly the lithium ions produced in equilibrium *a* would be more highly solvated than would sodium ions because of their smaller atomic radius and the more basic nature of the solvent (RNH_2 *vs.* NH_3). As a consequence of this higher concentration, the intermediate is protonated rapidly by the solvent, forming 1,4-dihydro products and a lithium alkylamide. The latter, because of its high solubility and strongly basic nature, readily can cause isomerization of the 1,4-products to conjugated dienes which are then reduced further by the reagent.

Two pieces of evidence indicate the 1,4-nature of the lithium-amine reductions. Anisole was treated with two equivalents of lithium, and the mixture was hydrolyzed quickly and worked up. Ultraviolet absorption indicated that 47% of the product was 2,3-dihydroanisole and 53% was the 2,5-isomer (*1*). Thus, even under the favorable isomerizing conditions which prevailed, a preponderance of the 1,4-isomer

was observed. The reduction of 2,3-dimethyl-1,3-butadiene gave almost exclusively 2,3-dimethyl-2-butene (*2*). That this compound resulted from a 1,4-reduction was indicated when an authentic sample of the 1-olefin was not isomerized appreciably under the reaction conditions of the reduction.

The importance of the isomerizing potential of the lithium-amine system was demonstrated by 1,4,5,8-tetrahydronaphthalene. Even at dry ice temperatures this compound was isomerized, at least in part, to a conjugated system by the lithium alkylamides produced in the lithium-amine reductions. But even a saturated solution of sodium amide in liquid ammonia was not as effective an isomerizing agent at −78°C., as judged by an ultraviolet absorption spectrum of the product (*2*).

When *tert*-butylbenzene was reduced with the lithium-amine reagent, a mixture of mono-olefins was produced (*2*). But the reduction of toluene under comparable conditions gave almost exclusively 1-methylcyclohexene. This difference in product may be associated with the inability of the basic media to effect isomerization of the olefin mixture to the more thermodynamically stable 1-isomer in the presence of the bulky *tert*-butyl group.

Experimental

The general reduction procedure employed in earlier work (*13*) was used throughout.

1,2,3,4-Tetrahydrofluorene. The crude product from the reduction of fluorene was recrystallized twice from 95% ethanol. An 83% yield of material melting at 55–6°C. was realized (literature 57°C.). A picrate melted at 71–2°C. (literature 72°C.). The infrared spectrum of the 1,2,3,4-tetrahydrofluorene indicated the presence of an aromatic ring (peak at 6.25 microns) and of a double bond conjugated with an aromatic ring (peak at 6.15 microns).

2,3-Dimethyl-2-butene. 2,3-Dimethylbutadiene (17.1 grams; 0.207 mole) was reduced in conventional fashion. Fractionation of the product yielded 5.99 grams, boiling point, 70–4°C., n_D^{20}, 1407; 1.8 grams, boiling point 75–9°C., n_D^{20} 1.409; and higher boiling material. All fractions boiling above 70°C. gave a solid bromine addition compound which is characteristic of 2,3-dimethyl-2-butene but not of the 1-isomer. 2,3-Dimethyl-2-butene has a boiling point of 72–3°C. (*9*), n_D^{20} 1.411. 2,3-Dimethyl-1-butene boils at 55°C. and has an index of refraction at 20°C. of 1.389 (*9*). An authentic sample of 2,3-dimethyl-1-butene (4.5 grams) was stirred for 30 minutes with a solution of lithium methylamide in methylamine. After working up the product, little if any isomerization occurred. The recovered material boiled at 55–7°C. (n_D^{20} 1.3904).

Isomerizations of 1,4,5,8-Tetrahydronaphthalene. An authentic sample of 1,4,5,8-tetrahydronaphthalene (melting point 56°C.) was prepared by the method of Hückel (*7*). The ultraviolet spectrum of this compound (0.001*M* solution in 95% ethanol) showed no peaks for a conjugated or aromatic system.

Lithium Methylamide. A 3-necked flask (200 ml.) was fitted with a dry ice condenser, a stirrer, and a Drierite–sodium hydroxide drying tube; 100 ml. of methylamine was condensed in this, and 0.14 gram of lithium and 4 grams of benzene were added. After all the lithium had reacted, the solution was cooled with a dry ice bath (−78°C.). To the cooled solution, 2.44 grams of 1,4,5,8-tetrahydronaphthalene in 20 ml. of ether was added. In about 15 minutes, the solution took on a red color which deepened toward the violet. After 1.5 hours, the mixture was hydrolyzed with about 100 ml. of water. The reaction product was extracted with several portions of ether. The extracts were washed with water and dried over Drierite. The ether was evaporated and the residue was placed under 5 mm. of pressure at room temperature to remove residual volatile material; 1.9 grams of hydrocarbon was obtained, melting point 47–51°C. An ultraviolet spectrum showed moderate absorption in the areas of conjugated double bonds (Table I).

Table I. Isomerization of 1,4,5,8-Tetrahydronaphthalene

Base System[a]	Sample Wt., G.	Temp., °C.[b]	Time, Hr.	M.P. Prod., °C.	$\epsilon^c \times 10^{-3}$ 221 mμ	266 mμ
$LiMeNH—MeNH_2$	1.0	−36	1.0	liq.	15.10	1.925
	2.4	−78	1.5	47–51	4.86	0.385
$NaNH_2—NH_3$	1.0	−36	1.0	38–43	14.00	1.200
	0.64	−78	1.5	54–5	1.89[d]	0.040

[a] Base concentration about 0.58*M*; solvent volume, about 100 ml.
[b] Bath temperature.
[c] ϵ = extinction coefficient; cell length, 1 cm.; hydrocarbon concentration, $10^{-3}M$.
[d] Based on an inflection point rather than a peak.

As above, lithium metal reacted with benzene to prepare lithium methylamide. The amide solution was evaporated to dryness at room temperature and 10 mm. to remove hydrocarbons. Then 100 ml. of methylamine was condensed in the flask, an external cooling bath of 1,2-dichloroethane slush (−36°C.) was applied, and 1 gram of 1,4,5,8-tetrahydronaphthalene in 20 ml. of ether was added. The reaction was allowed to proceed 1 hour before hydrolyzing and working up as above. A pale amber liquid was obtained which was dried at 10 mm. to remove all volatile material. An ultraviolet spectrum showed very extensive absorption in areas expected for conjugated systems (Table I).

Sodium Amide. In the apparatus described above, 100 ml. of liquid ammonia was condensed; 1.36 grams of sodium and a few crystals of hydrated ferric nitrate were added to the ammonia solution. When the sodium had dissolved completely to form a gray suspension of sodium amide, the mixture was cooled with a dry ice bath (−78°C.). To the cooled solution was added 0.64 gram of 1,4,5,8-tetrahydronaphthalene in 20 ml. of ether. After stirring 1.5 hours, about 100 ml. of water was added, and the mixture was worked up as described above. There was obtained 0.31 gram of pale yellow solid, melting point 55–5.5°C. An ultraviolet spectrum of this material showed very little absorption in the areas expected for conjugated systems (Table I).

A solution of sodium amide in liquid ammonia was prepared as above. After cooling the amide solution to −36°C. in a bath of 1,2-dichloroethane slush, 1.0 gram of 1,2,3,4-tetrahydronaphthalene in 20 ml. of ether was added. The reaction was allowed to proceed 1 hour before hydrolyzing and working up. A low melting, pale yellow solid, melting point 38–43°C., was obtained. The ultraviolet spectrum of this solid showed extensive absorption in the areas expected for conjugated systems (Table I).

Preparation of 3-Methylcyclohexene. Methylmagnesium bromide, prepared from 13 grams (0.53 gram-atom) of magnesium turnings and excess methyl bromide in 200 ml. of ethyl ether solvent, was decanted into a dropping funnel. From this funnel, the Grignard reagent was added over 1 hour to a refluxing solution of 50 grams of 3-bromocyclohexene in 100 ml. of ether. After standing overnight, the reaction mixture was hydrolyzed with water and acetic acid and extracted with ether. The ether extracts were neutralized, dried over anhydrous magnesium sulfate, and distilled, producing 11.1 grams of 3-methylcyclohexene, boiling point 48–49°C. (121 mm.), n_D^{20} 1.4430.

Reduction of *tert*-Butylbenzene. The reduction was carried out utilizing standard reduction conditions. Fractionation of the product gave an 84% yield of a hydrocarbon mixture boiling at 168–9°C. (n_D^{20} 1.460). A nitrosochloride derivative melted at 100°C. (dec.) and did not depress the melting point of a nitrosochloride derivative prepared from authentic 1-*tert*-butylcyclohexene (*6*).

When the crude reduction mixture was oxidized with potassium permanganate, a small amount of acid (neutralization equivalent 99) melting point 114–5°C. was isolated. This corresponded to β-*tert*-butyladipic acid (melting point 115–6°C.; neutralization equivalent 101) (*8*). Thus the presence of 4-*tert*-butylcyclohexene in the olefin mixture was indicated. An ultraviolet spectrum indicated the presence of un-

reduced *tert*-butylbenzene as well as the probable presence of 3-*tert*-butylcyclohexene.

Attempted Isomerization of 3-Methylcyclohexene and 3-*tert*-Butylcyclohexene. 3-Methylcyclohexene (n_D^{20} 1.4430) was refluxed 1.5 hours with lithium methylamide in methylamine. When the product was worked up and fractionated, a sizable portion boiled at 104–8°C. (n_D^{20} 1.451).

The above reaction was repeated using 3-*tert*-butylcyclohexene (n^{20} 1.4591; boiling point 67°C.) under exactly comparable conditions. The bulk of the product boiled at 66°C. (n_D^{20} 1.4590), indicating that little isomerization to the 1-isomer had occurred.

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Organosodium Compounds for Preparation of Other Carbon-Metal Bonds

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The history and preparation of organometallic compounds are discussed. The reactions of organosodium compounds with various metal chlorides are given, including the conversion of organosodium compounds to the corresponding Grignard reagents by reaction with magnesium chloride. Although only a few of the organometallic compounds possible by reaction of an organosodium compound with a metal halide have been prepared, the way has been opened to economical, commercial syntheses of materials that are increasingly important in many fields.

Organometallic compounds react with other metals or metal halides to produce compounds with a new carbon-metal bond. This type of reaction was used in the late 19th century after Frankland discovered the first true organometallic compounds, diethylzinc (*3*) and methylmercuric iodide (*12*), in 1849 and 1853, respectively. Other derivatives of zinc and mercury were prepared in subsequent years, but it was not until 1900, when Grignard (*7*) isolated the first organomagnesium compound, that the organometallic field received a tremendous impetus. The reaction of an organozinc, mercury, or magnesium compound with a metal, metal halide, or alkoxide to form a new organometallic compound was used considerably more after that time.

Two general reactions have been useful. The first comprises the reduction of an organometallic compound by another metal:

$$RM + M' \rightarrow RM' + M \quad (1)$$

A specific illustration of this reaction is the well known synthesis of an organosodium compound from the corresponding organomercury derivative:

$$R_2Hg + 3Na \rightarrow 2RNa + Na(Hg) \quad (2)$$

The second general reaction is the simple displacement reaction between an organometallic compound and the salt of another metal:

$$RM + M'X \rightarrow RM' + MX \quad (3)$$

This may be illustrated by the classical conversion of a Grignard reagent to an organocadmium compound:

$$2RMgCl + CdCl_2 \rightarrow R_2Cd + 2MgCl_2 \quad (4)$$

For Reaction 1 to proceed to the right, M′ must be a more active metal than M: If M and M′ are in different groups in the periodic table, M′ must lie to the left of M; whereas if M′ and M belong to the same periodic family, M′ must lie below M. Thus, a Grignard reagent should undergo reaction with calcium or sodium, but not with beryllium or aluminum.

The reverse is true regarding Reaction 3. For the displacement to take place, M′ must be less active than M. The Grignard reagent should react with beryllium chloride or aluminum chloride, but not with calcium chloride or sodium chloride. In theory, Reactions 1 and 3 provide for the replacement of a metal in an organic compound by any other metal on the periodic table.

Organoalkali Compounds

The formation of compounds containing new carbon-metal bonds through the use of organoalkali compounds is a recent development dating from the discovery in 1930 (Table I) by Ziegler and Colonius (*14*) of the direct preparation of organolithium

Table I. Historical Development of Organometallic Compounds

R_2Zn	1849	(*3*
RHgI	1853	(*12*)
RMgX	1900	(*7*)
RLi	1930	(*14*)
	1932	(*6*)
RNa (first)	1933	(*5*)
ϕNa (first)	1935	(*1*)
Fine Na sand + high speed stirring	1937	(*9*)
Na dispersions	1951	(*8*)
ϕNa (theoretical yield)	1954	(*10*)
NaC_8Na (first large commercial use)	1955	(*2*)

compounds from organic halides and metallic lithium. The use of organolithium compounds as a laboratory tool for preparation of alkyl and aryl derivatives of boron, aluminum, silicon, germanium, lead, tin, antimony, and bismuth, has been studied extensively by Gilman and others during the past 20 years.

The early chemical literature contained abundant references to the transitory existence of organosodium compounds as intermediates in Wurtz reactions, but the direct preparation of an organosodium compound from sodium and an alkyl or aryl halide was believed impossible. Accordingly, the first preparation of such compounds involved the interaction of sodium with dialkylmercury or dialkylzinc. This technique was used until 1933, when Gilman and Wright (*5*) prepared an organosodium compound (3-furylsodium) directly from an organic halide (3-chlorofuran) and metallic sodium. The first preparation of phenylsodium from chlorobenzene and sodium was reported by Bockmühl and Ehrhart (*1*). Thereafter, a number of investigators, chiefly Morton and Gilman, reported the preparation of a variety of organosodium compounds from organic chlorides and sodium metal.

Until Morton and Fallwell (*9*) introduced the use of a fine sodium sand, or crude dispersion (100- to 500-micron sodium particles), coupled with high speed stirring, the preparation of organosodium compounds from alkyl or aryl chlorides and sodium was a tedious, time-consuming process which often resulted in low yields. The studies of Hansley (*8*) on preparation and use of finely dispersed sodium (10 to 30 microns) in the formation of phenylsodium in 90% yields opened a new era in organosodium chemistry. Further studies in the authors' laboratories (*10*) have shown that phenylsodium and benzylsodium can be prepared in nearly quantitative yields by the use of carefully controlled reaction conditions which include the presence of a slight excess of freshly dispersed sodium. The reaction between chlorobenzene and sodium under these conditions is immediate and complete; 1 mole of phenylsodium may be prepared in only 20 minutes. This reaction is easily adapted to larger

scale and is being used industrially on a plant scale. Other organosodium compounds also are being used in pilot plant and plant scale. The largest commercial plant utilizing organosodium compounds is operated at Tuscola, Ill., by the U. S. Industrial Chemicals Co., Division of National Distillers and Chemical Corp. This plant uses disodio-octadiene, an organosodium compound made directly from butadiene and sodium (*2*), in the preparation of Isosebacic acid, a mixture of 10-carbon dibasic acids.

Many laboratories utilize organosodium compounds in organic synthesis, as no change in the organometallic intermediate need be made in scale-up to pilot plant or plant. Frequently, the handling of organosodium compounds is safer and more convenient than handling Grignard reagents or organolithium compounds, where large quantities of ether usually are required.

Reaction of Organosodium Compounds

Although many metal halides such as titanium, zirconium, boron, and aluminum may be reduced to metals with sodium, these same metal halides react with organosodium compounds to form new carbon-metal bonds. Organosodium compounds may react with the halides or alkoxides of lithium, magnesium, mercury, boron, aluminum, silicon, germanium, tin, lead, titanium, zirconium, phosphorus, and iron. The organometallic derivatives in Table II can be prepared from organomagnesium, lithium, or sodium compounds.

Table II. Reaction of Organosodium Compounds with Metal Salts

Halide or Alkoxide	Derivative
LiCl	RLi
$HgCl_2$	R_2Hg
BCl_3	R_3B
$AlCl_3$	R_3Al
$SiCl_4$	R_2SiCl_2
$GeCl_4$	R_4Ge
$SnCl_4$	R_2SnCl_2
$PbCl_4$	R_4Pb
$TiCl_4$	R_2TiCl_2 (cyclopentadienyltitanium dichloride)
$ZrCl_4$	R_2ZrCl_2 (cyclopentadienylzirconium dichloride)
PCl_3	R_3P
$FeCl_2$	R_2Fe (ferrocene)

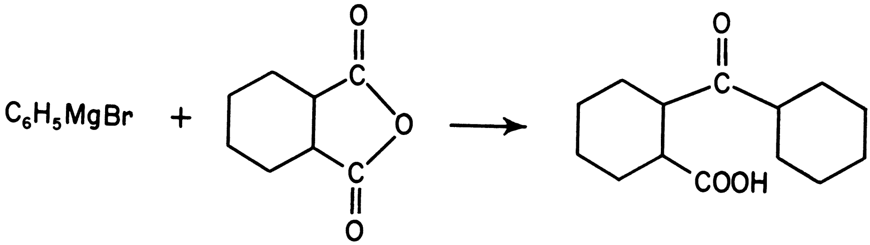
Magnesium Chloride. Work was initiated in the authors' laboratories to study the conversion of organosodium compounds to the corresponding Grignard reagents:

$$RNa + MgCl_2 \rightarrow RMgCl + NaCl \quad (5)$$

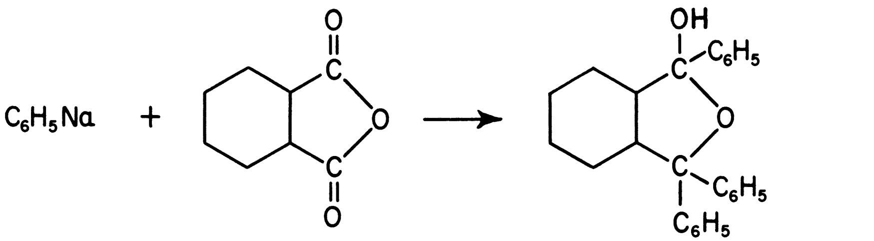
Until recently, the reaction of an organosodium compound with magnesium chloride had no potential value, because usually the Grignard reagents were more easily prepared than the corresponding organosodium compounds. Developments in the ease of preparation of organosodium compounds, however, have changed this situation. There are cases where organosodium compounds can be prepared from starting materials which yield Grignard reagents only with difficulty. For example, organic chlorides and particularly certain aromatic or heterocyclic chlorides react very sluggishly with magnesium, but yield organosodium compounds readily. As a result, many Grignard reagents which have been prepared from expensive iodides or bromides can be obtained by this method from the less expensive chlorides, often in higher yields than from the reaction of a halide with metallic magnesium. Other organosodium compounds, such as disodio-octadiene, obtained through reactions which are completely unknown in the field of organomagnesium chemistry, can be converted to Grignard reagents which had been unattainable.

Often it is advantageous to convert an organosodium intermediate to the corresponding Grignard reagent prior to further reaction. In certain substitution reactions, the high order of reactivity of the organosodium compound leads to undesirable side reactions of which the Grignard reagent is not capable. For exam-

ple, the reaction of a Grignard reagent with acetic anyhdride may be sufficiently controlled to produce a methyl ketone in excellent yield. The corresponding reaction with an organosodium compound inevitably produces a significant quantity of tertiary alcohol. Similarly, *o*-benzoylbenzoic acid may be prepared in good yield through the action of phenylmagnesium chloride on phthalic anhydride (Reaction 6). The corresponding reaction with phenylsodium cannot be brought under control, and triphenyldihydroisobenzofuran is the chief product (Reaction 7):



(6)



(7)

Another example is the reaction of an organometallic compound with chloramine to yield a primary amine. Present indications are that this coupling reaction proceeds more smoothly with a Grignard reagent than with an organosodium compound.

$$RMgBr + ClNH_2 \rightarrow RNH_2 \qquad (8)$$

There are other reactions in which the Grignard reagent gives an entirely different product than does the organosodium compound—e.g., in reaction with benzalacetophenone. An organosodium compound adds to this material to yield the expected tertiary alcohol exclusively. The Grignard reagent, on the other hand, yields an alkylated ketone:

$$\phi CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\phi + RNa \rightarrow \phi CH{=}CH{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}{-}\phi \qquad (9)$$

$$\phi CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\phi + RMgX \rightarrow \phi{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\phi \qquad (10)$$

To determine if magnesium chloride would react with an RNa compound, it was first established that the desired metal-metal interconversion reaction would take place to form the RMgCl derivative. When phenylsodium is refluxed with toluene, benzylsodium is formed quantitatively, and carbonation gives phenylacetic acid. Phenylmagnesium chloride, on the other hand, undergoes no reaction on refluxing with toluene, and carbonation of such a mixture gives only benzoic acid.

$$\phi Na \xrightarrow[\text{reflux}]{\text{toluene}} \phi CH_2Na \xrightarrow{CO_2} \phi CH_2COONa \qquad (11)$$

$$\phi MgCl \xrightarrow[\text{reflux}]{\text{toluene}} \phi MgCl \xrightarrow{CO_2} \phi COOMgCl \qquad (12)$$

Accordingly, a suspension of phenylsodium in toluene was prepared and stirred at room temperature for 2 hours with magnesium chloride. The reaction mixture was heated under reflux for 2 hours. Carbonation on dry ice produced only benzoic acid, indicating that no benzyl organometallic had been formed. Clearly, phenylmagnesium chloride had been produced.

Similarly, a suspension of disodio-octadiene in dimethyl ether reacted with tritane to produce tritylsodium (triphenylacetic acid on carbonation) before treatment with magnesium chloride, but underwent no reaction with tritane after the magnesium chloride treatment. Thus, the organometallic compound was assumed to be bischloromagnesio-octadiene, because the acids obtained on carbonation were mixed 10-carbon dibasic acids.

$$NaC_8Na + \phi_3CH \longrightarrow \phi_3CHNa \xrightarrow{CO_2} \phi_3CCOONa \quad (13)$$

$$NaC_8Na + MgCl_2 + \phi_3CH \longrightarrow ClMgC_8MgCl \xrightarrow{CO_2} \text{Mixture of 10-carbon acids} \quad (14)$$

Butylsodium gave a similar reaction with tritane without the magnesium chloride, but only valeric acid was isolated on carbonation when magnesium chloride was present.

$$BuNa + \phi_3CH \rightarrow \phi_3CHCOONa \quad (15)$$

$$BuNa + MgCl_2 + \phi_3CH \rightarrow BuCOOMgCl \quad (16)$$

Certain organometallic reactions require relatively high temperatures and some Grignard reagents are more stable than some organosodium compounds at temperatures above 100°C. In these cases, it would be advantageous to prepare the organosodium compound first in a hydrocarbon medium and then react with anhydrous magnesium chloride. Several advantages are achieved: Certain economies are realized with respect to the comparison between sodium and magnesium; higher yields may be realized; and the Grignard reagent is prepared essentially in a hydrocarbon rather than in an ether medium. Should an ether reaction medium be desired for later reactions, the hydrocarbon solvent may be replaced with an ether after formation of the Grignard reagent.

Lithium Chloride. In 1940 Gilman and Swiss (*4*) suggested that the reaction between an organosodium compound and lithium chloride would yield an organolithium compound. Recent work in the authors' laboratories has shown that such a reaction does take place. Thus, an economical route has been opened to the preparation of organolithium compounds in hydrocarbon media.

Aluminum Chloride. The reaction between an organosodium compound and aluminum chloride has not been reported previously. An organosodium compound will react with aluminum chloride only if a small amount of ether is present. In benzene or aliphatic hydrocarbon media, there is no apparent reaction between phenylsodium and aluminum chloride. Similarly, butylsodium does not react with

Table III. Newer Reactions of Organosodium Compounds with Metal Halides

RNa	Metal Halide	Product	Yield, %		
			0°C.		−40°C.
ϕNa	BCl_3	ϕ_3B		50	
BuNa	$AlCl_3$	Bu_2AlCl (etherate)		45	
ϕNa	$SiCl_4$	$\phi SiCl_3$	17.2		38.2
		ϕ_2SiCl_2	21.3		14.4
		ϕ_4Si	29.3		34.5
ϕNa	CH_3SiCl_3	ϕCH_3SiCl_2		45	
BuNa	$SnCl_4$	Bu_2SnCl_2		41	
C_5H_5Na	$TiCl_4$	$DCPTICl_2$ $(C_5H_5)_2TiCl_2$		90	
ϕCH_2Na	PCl_3	$(\phi CH_2)_3P$		84.1	

aluminum chloride in hexane. If a small amount of ether is added before reaction with aluminum chloride, or if the aluminum chloride is first dissolved in ether and then added to the butylsodium, dibutylaluminum chloride etherate may be produced in 45% yield (Table III).

Boron Trichloride and Silicon Tetrachloride. Organosodium compounds react with boron trichloride to give, in the case of phenylsodium, triphenylborine (50% yield). They react with silicon tetrachloride to give phenylsilicon trichloride, diphenylsilicon dichloride, or higher phenylated silicon compounds. The particular compound produced can be controlled somewhat by the mode of addition, the temperature of reaction, and the excess of silicon tetrachloride. By adding phenylsodium to a large excess of silicon tetrachloride at −40°C., a 38% yield of phenylsilicon trichloride may be produced. In addition, 14% diphenylsilicon dichloride and 35% tetraphenylsilane are obtained. At 0°C., 17% of the monophenyl derivative, 21% of the diphenyl derivative, and 20% tetraphenylsilane are produced. The phenylsilicon trichloride may be separated from the other products and converted to additional diphenylsilicon dichloride by the addition of more phenylsodium. It is also possible to prepare phenylmethylsilicon dichloride in 45% yield by the reaction of phenylsodium with an excess of methylsilicon trichloride. Other mixed silicon compounds can be prepared in a similar fashion.

Stannic Chloride. Organotin compounds also have been prepared from butylsodium and stannic chloride. Advantage may be taken of the ease of disproportionation of organotin compounds by preparing tetrabutyltin first (41% yield) and then converting to dibutyltin dichloride (95% yield) by reaction with the proper quantity of stannic chloride. It is also possible to prepare dibutyltin dichloride (40% yield) or other tin compounds directly from the organosodium compound and the proper molar equivalent of stannic chloride, but in some cases yields are lower.

Titanium Tetrachloride. Dicyclopentadienyltitanium dichloride has been prepared from dicyclopentadienyllithium or sodium and titanium tetrachloride (*1 13*). The authors noted that this compound may be prepared in 90% yield from cyclopentadienylsodium and titanium tetrachloride.

Phosphorus Trichloride. Organophosphorus compounds have been prepared by reaction of phosphorus trichloride with an organosodium compound. The reaction of benzylsodium and phosphorus trichloride results in 84% yield of tribenzylphosphorus. Triphenylphosphine has been produced in semicommercial quantities by a similar reaction.

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Some Aspects of Sodium Acetylide Chemistry

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The synthesis, stability, and reactions of sodium acetylide are discussed. The procedure presented for the preparation of sodium acetylide gives a more reactive material than other methods. This involves the reaction of acetylene with sodium dispersed in mineral oil.

Sodium acetylide has intrigued industrial chemists for many years. It is difficult to envision another organometallic compound which can rival sodium acetylide's unique combination of low molecular weight and polyfunctional character. Because sodium acetylide can be easily prepared from cheap and readily available starting materials, the chemistry of this versatile compound has been studied in many industrial and academic laboratories.

Synthesis

Sodium acetylide may be prepared by the reaction of acetylene with molten sodium (*12*), sodium in liquid ammonia (*20*), sodium dispersed in a hydrocarbon (*8*), sodium-coated solids (*4–6*), sodamide (*16*, *17*), or sodium hydride (*13*). In the laboratory, the most common procedure has been the use of sodium in liquid ammonia (*14*). Sittig stated that the most practical route involves the reaction of acetylene with sodamide (*19*). In the authors' experience, the sodium dispersion route is far superior to the other methods. Even though part of the acetylene is reduced by the hydrogen liberated by the reaction with sodium (Equation 1), this is outweighed by the additional step needed in the sodamide process to convert sodium to sodamide.

$$2HC{\equiv}CH + 2Na \rightarrow 2HC{\equiv}CNa + H_2 \qquad (1a)$$

$$HC{\equiv}CH + H_2 \rightarrow H_2C{=}CH_2 \qquad (1b)$$

$$3HC{\equiv}CH + 2Na \rightarrow 2HC{\equiv}CNa + H_2C{=}CH_2 \qquad (1\ \text{over-all})$$

The authors found that less than 1 out of 3 moles of acetylene is reduced during the reaction with a sodium dispersion. The stoichiometry is represented best by Equation 2.

$$2.8HC{\equiv}CH + 2Na \rightarrow 2HC{\equiv}CNa + 0.7H_2C{=}CH_2 + 0.1CH_3CH_3 + 0.1H_2 \qquad (2)$$

The authors' procedure involves passing acetylene through a rapidly stirred dispersion of sodium in mineral oil. The temperature should be between 110° and 150°C., and the rate of acetylene addition is determined by the efficiency with which

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the heat of reaction can be removed. In the laboratory, a dispersion of 1.5 moles of sodium in 300 ml. of mineral oil (Bayol D, Esso Standard Oil Co.) is used in a 1-liter creased flask with a high speed Stir-O-Vac (Lab-line, Inc., Chicago 22, Ill.) stirrer. Under these conditions, with an acetylene flow rate of 1500 ml. per minute, reaction is complete in about 2 hours.

The flask is cooled by external application of an air stream during the first part of the reaction, and external heat is applied toward the end of the reaction to maintain the temperature at 150°C. Yields based on sodium are essentially quantitative, and the acetylene conversion is about 20%. It should be possible in commercial operation, either through the use of a tubular reactor or by acetylene recycle, to increase acetylene conversion above 60%.

Stability

The sodium acetylide prepared in this manner is a finely divided white solid. It is preferably used as a mineral oil suspension, with no attempt to isolate the solid, because sodium acetylide is easily ignited when dry. In mineral oil suspension, sodium acetylide is protected from oxidation, and is thermally stable up to about 180°C. When heated above that temperature, disproportionation takes place. Acetylene is liberated and disodium acetylide is formed in accordance with Equation 3.

$$2HC{\equiv}CNa \rightarrow NaC{\equiv}CNa + HC{\equiv}CH \quad (3)$$

This disproportionation reaction is catalyzed by bases such as sodamide, sodium hydride, and even sodium. The mechanism of catalysis may involve a sequence of reactions such as Equation 4.

$$HC{\equiv}CNa + NaNH_2 \rightarrow NaC{\equiv}CNa + NH_3 \quad (4a)$$

$$HC{\equiv}CNa + NH_3 \rightarrow HC{\equiv}CH + NaNH_2 \quad (4b)$$

$$2HC{\equiv}CNa\ (+ NaNH_2) \rightarrow NaC{\equiv}CNa + HC{\equiv}CH\ (+ NaNH_2) \quad (4\text{ over-all})$$

Catalysis by sodium is especially important, as sodium acetylide is usually contaminated by traces of unreacted sodium. The authors have prepared occasional samples of sodium acetylide which were thermally stable above 200°C. These samples probably contained little or no unreacted sodium. A highly purified sample of sodium acetylide, if it could be prepared, might be thermally stable to much higher temperatures.

A kinetic study revealed that the disproportionation of sodium acetylide is autocatalytic. As shown by Figure 1, the rate is rather rapid at first, but soon falls

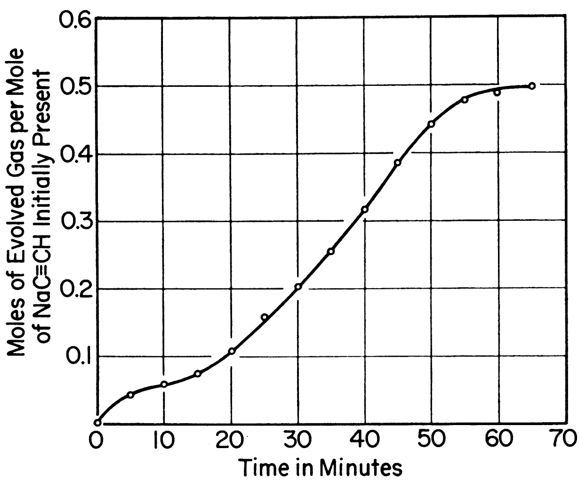


Figure 1. Rate of sodium acetylide disproportionation

off, and then slowly increases until near the end of the reaction. Behavior of this type has been described by Garner (*9*) in terms of crystal nucleation theory. Thus, the initiation of the reaction is presumed to involve the formation of disodium acetylide nuclei at certain localized spots, followed by relatively rapid growth of the nuclei. The rapid gas evolution during the first 10% of the reaction may be attributed to fast crystal growth on the surface of the sodium acetylide particles because of the ease of acetylene escape from the surface.

Reactions

Sodium acetylide reacts with aldehydes and ketones to produce acetylenic glycols (*3*, *18*), as illustrated in Equation 5.

$$HC{\equiv}CNa + R_2C{=}O \rightarrow R_2C(ONa){-}C{\equiv}CH \rightarrow R_2C(OH){-}C{\equiv}CH \qquad (5)$$

This reaction is of commercial importance in the synthesis of hypnotic drugs and a number of unsaturated alcohols related to vitamin A.

Also of commercial interest is the reaction of sodium acetylide with dimethyl sulfate to give methylacetylene (propyne). Under the usual conditions (*2*), sodium acetylide reacts with only one of the methyl groups of dimethyl sulfate (Equation 6).

$$HC{\equiv}CNa + (CH_3O)_2SO_2 \rightarrow HC{\equiv}C{-}CH_3 + CH_3OSO_2ONa \qquad (6)$$

By operating at a higher temperature, it is possible to utilize both methyl groups (*1*, *15*) (Equation 7).

$$2HC{\equiv}CNa + (CH_3O)_2SO_2 \rightarrow 2HC{\equiv}C{-}CH_3 + Na_2SO_4 \qquad (7)$$

Thus when dimethyl sulfate is added at 80° to 95°C. to a mineral oil (or xylene) suspension of sodium acetylide and the evolved propyne is collected in a dry ice trap, the reaction follows the path described by Equation 7 and is complete in about 2 hours. The yield of propyne, after fractionation, is about 75%, and an additional 10% of 2-butyne can be isolated. The butyne presumably is formed by the sequence of reactions shown by Equations 8a and b.

$$HC{\equiv}CNa + CH_3{-}C{\equiv}CH \rightarrow HC{\equiv}CH + CH_3{-}C{\equiv}CNa \qquad (8a)$$

$$2CH_3{-}C{\equiv}CNa + (CH_3O)_2SO_2 \rightarrow 2CH_3{-}C{\equiv}C{-}CH_3 + Na_2SO_4 \qquad (8b)$$

At the temperatures employed in this reaction, sodium methyl sulfate should be in equilibrium with an appreciable concentration of dimethyl sulfate and sodium sulfate:

$$2CH_3OSO_2ONa \rightleftharpoons (CH_3O)_2SO_2 + Na_2SO_4 \qquad (9)$$

Removal of dimethyl sulfate by reaction with sodium acetylide should drive the equilibrium to the right and result in the utilization of both methyl groups.

Perhaps the most important reaction of sodium acetylide is its conversion to the sodium salt of propiolic acid by treatment with carbon dioxide:

$$HC{\equiv}CNa + CO_2 \rightarrow HC{\equiv}C{-}COONa \qquad (10)$$

Propiolic acid, by virtue of its trifunctional character, is a promising synthetic intermediate. Typical of its many reactions is an oxidative coupling to a polyunsaturated adipic acid derivative (*7*), from which highly halogenated dicarboxylic acids may be prepared:

$$2HC{\equiv}C{-}COOH \xrightarrow{[O]} HOOC{-}C{\equiv}C{-}C{\equiv}C{-}COOH \rightarrow X_2HOOC{-}(CX_2)_4{-}COOH \qquad (11)$$

As usually carried out, the reaction of carbon dioxide with sodium acetylide has been too slow for commercial application. Apparently the particle size, or other surface characteristics, of sodium acetylide prepared in liquid ammonia from either sodamide or sodium, is such that the rate of reaction is impractically slow. Jackson

and Vaughn (*10*) cite dioxane as a better solvent than liquid ammonia for the carboxylation of sodium acetylide, as the length of reaction using dioxane is reduced to 16 hours. Macallum (*11*) suggests replacing liquid ammonia with kerosine to reduce the reaction time to a minimum of 8 hours at 800 to 900 p.s.i.

The authors found that sodium acetylide prepared from sodium dispersed in mineral oil can be converted to sodium propiolate in 70% yield in 1 hour at 400 to 500 p.s.i. and 0° to 10°C. After acidification, propiolic acid can be isolated from aqueous solution by continuous extraction with ether, using about 10 volumes of ether per volume of water, or by continuous countercurrent extraction with about 3 to 5 volumes of isopropyl acetate or methyl isobutyl ketone. This demonstration of the reactivity of sodium acetylide provides convincing evidence that the use of sodium dispersions is the most practical method for the preparation of sodium acetylide.

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Grignard Reagents

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A description of the application of the classical Grignard reaction to industrial syntheses in batchwise equipment is given. The discussion excludes reactions which involve the intermediate formation of other organometallic compounds from the Grignard reagent and applies particularly to the synthesis of alcohols from Grignard reagents and carbonyl compounds. The formation of Grignard reagent, reaction with a carbonyl compound, hydrolysis of the complex, and isolation of the product are discussed with reference to a fairly detailed flow sheet of an operating plant. Other processes proposed for the industrial application of the Grignard reaction are mentioned briefly. Also included is a general discussion of the advantages and disadvantages of the Grignard reaction as an industrial process, with some indication of the economics of the process.

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Although the Grignard reaction has been in constant widespread use since its discovery by Victor Grignard in 1900 (*7*), it has only fairly recently come into prominence as an industrial tool. Modern developments in the fields of hormones, vitamins, perfumes, and silicones have led to increasing commercial application of this versatile and precise reaction, and in recent years custom manufacturing facilities and Grignard solutions themselves have become commercially available.

The scope of the Grignard reaction is so well known and has been so well reviewed that no attempt is made here to discuss it in detail. Gilman (*6*), Runge (*15*), and Krause and von Grosse (*11*) have reviewed the chemistry of organometallic compounds. Most recently Kharasch and Reinmuth (*10*) have published an excellent treatise which very thoroughly discusses the reactions of Grignard reagents from both theoretical and practical laboratory standpoints. The technological aspects of the Grignard process have, however, been less extensively treated (*1, 22*). The purpose of this paper is, therefore, to describe a simple commercial-scale plant for carrying out the Grignard reaction and to discuss some of the advantages and disadvantages of this reaction in commercial operations.

The plant shown in Figures 1 and 2 was set up in 1953 to carry out custom synthesis via the Grignard reaction and to produce Grignard reagents for sale as such. It has been in successful intermittent operation ever since. In it the Grignard reagent is prepared and allowed to react with a carbonyl or other reactive compound, the resultant complex is hydrolyzed, and the final product is freed of solvent. Numerous other reactions of the Grignard reagent can be carried out in the same or slightly modified equipment. However, because the reaction of the reagent with carbonyl

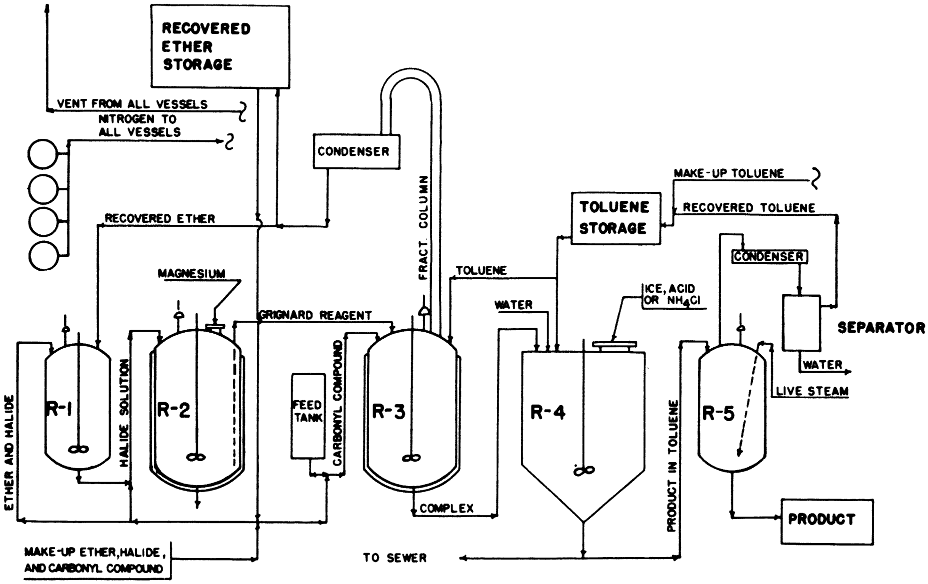


Figure 1. Flow diagram of plant for carrying out Grignard reactions

Vessel schedule

R-1	500 gal.
R-2	650 gal.
R-3	650 gal.
R-4	1100 gal.
R-5	300 gal.
Storage tanks	1000 gal.

compounds is of wide utility, that reaction was chosen for discussion here. It is felt that the principles involved are generally applicable.

The basic reactions involved are:

Formation of Grignard reagent

$$RX + Mg \rightarrow RMgX \quad (1)$$

Reaction with carbonyl compound

$$RMgX + R'COR'' \rightarrow R'{-}\overset{\displaystyle R''}{\underset{\displaystyle R}{C}}{-}OMgX \quad (2)$$

Hydrolysis of complex

$$R'{-}\overset{\displaystyle R''}{\underset{\displaystyle R}{C}}{-}OMgX + HOH \rightarrow R'{-}\overset{\displaystyle R''}{\underset{\displaystyle R}{C}}{-}OH + Mg(OH)X \quad (3)$$

Formation of Grignard Reagent

The Grignard reagent is usually prepared in the classic way by adding a solution of the organic halide in ether to a mixture of ether and magnesium turnings. The halide is dissolved in ether in the vessel, *R*-1, and the solution is then fed into *R*-2, which contains magnesium turnings and ether. Both *R*-1 and *R*-2 are purged with nitrogen before ether is introduced.

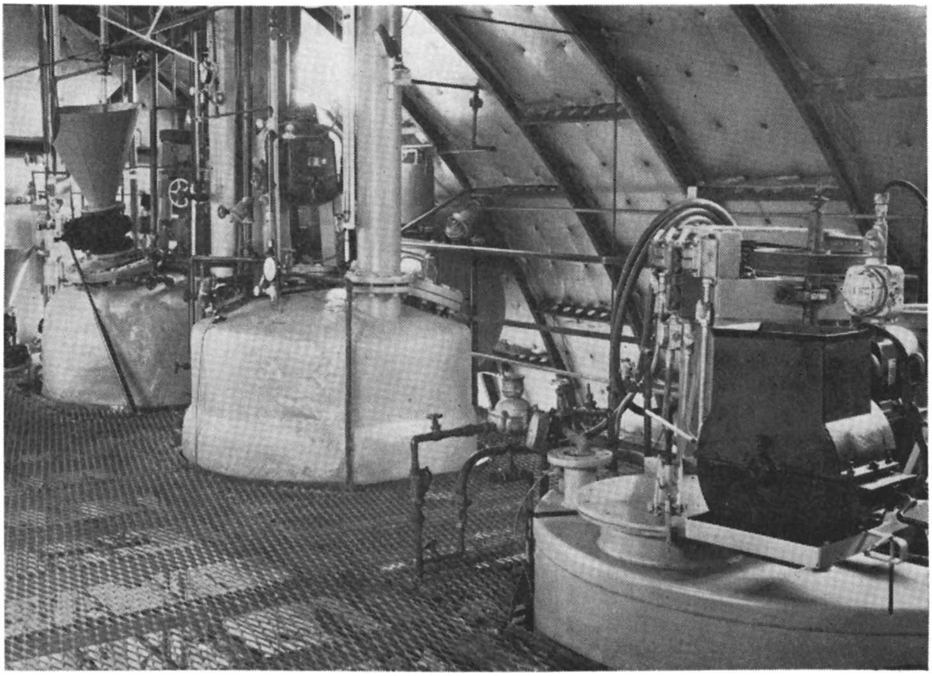


Figure 2. General view of Grignard reactor line

The chief problem in the formation of Grignard reagents results from the difficulty which is often encountered in starting the reaction. Hence, the literature contains a multitude of recommended procedures for initiating the Grignard reaction. Iodine, bromine, preformed Grignard reagent, silicate esters, and iodine-activated magnesium have been suggested. No method has been devised which will work in all cases. Some halides react readily, while others are extraordinarily difficult. It is, however, essential that a sustained reaction be initiated by the first portion of halide before further additions are made. Failure to observe this precaution may result in the build-up of such an excess of unreacted halide that the reaction, when it finally starts, may become so vigorous that the temperature cannot be controlled. A violent increase in pressure will result. Adequate explosion lines must therefore be provided on Grignard reactors as protection against such delayed reactions. Much of this hazard can be avoided by transferring the finished reagent to another vessel, *R*-3 in this case, for reaction with a carbonyl compound, but retaining an excess of activated magnesium in the reactor, *R*-2, to assist in starting the next reaction.

Efficient agitation is essential to the production of satisfactory yields of the Grignard reagent. By vigorous agitation and gradual addition of the halide, local overheating and consequent losses by Wurtz reaction and disproportionation are minimized.

In spite of its hazards, ethyl ether seems to be the most generally satisfactory solvent for preparing Grignard reagents. Higher boiling ethers, tetrahydrofuran, tertiary amines, and hydrocarbons have been recommended but in most cases its good solvent power, low cost, high commercial purity, and ease of recovery make ethyl ether the solvent of choice for Grignard reactions. The reaction is usually carried out under a pressure of about 20 pounds in order to raise the boiling point of ether to a temperature where jacket cooling is sufficient to prevent boiling. Higher temperatures, however, often lead to lower yields, presumably through the Wurtz and disproportionation reactions. Several factors must therefore be balanced to achieve optimum operating conditions in any particular case.

Recent reports by Normant (*12*) and by Ramsden and his associates (*13*), indicate that Grignard reagents may be prepared from relatively inert halides—e.g., vinyl and aryl chlorides—if tetrahydrofuran is used as the solvent. Previously these reagents could not be prepared in convenient ways, although several procedures (*3, 19, 20, 23*) which utilized no solvent other than excess halide had been reported for producing phenylmagnesium chloride.

The practical strength of Grignard reagents is determined largely by the nature of the halide. Thus methylmagnesium bromide can be made in good yield in $4M$ strength, while at about $3M$ strength the purity of phenylmagnesium bromide begins to deteriorate, because of the formation of excessive amounts of biphenyl by way of the Wurtz reaction:

$$2RX + Mg \rightarrow R_2 + MgX_2 \qquad (4)$$

Beyond $3M$ strength the Wurtz reaction appears to be the main reaction. Benzyl chloride likewise tends to undergo the Wurtz reaction at strengths in excess of about $1M$.

Chlorides, in general, suffer from the ether-insolubility of magnesium chloride etherate which arises from the Schlenk and Schlenk (*16*) equilibrium:

$$2RMgX \rightleftarrows R_2Mg + MgX_2 \qquad (5)$$

Thus even a $1M$ solution of methylmagnesium chloride deposits large quantities of magnesium chloride, and at higher strengths the mixture may become nearly solid. Benzylmagnesium chloride solutions also deposit magnesium chloride which, if allowed to stand, forms a solid cake. Because magnesium bromide is readily soluble in ether, bromides can usually be carried to higher strength than can chlorides. Fluorides usually do not enter into Grignard reactions, while iodides are seldom used because of high cost and excessive losses by way of the Wurtz reaction.

Other major side reactions are disproportionation, reaction with active hydrogen, and reaction with oxygen. The first of these may be represented by the equation:

$$2RX + Mg \rightarrow R_{(+H)} + R_{(-H)} + MgX_2 \qquad (6)$$

In the formation of several of the most useful reagents—e.g., methyl, benzyl, and phenyl—this reaction is not a factor because there is no opportunity for olefin, $R_{(-H)}$, formation. However, disproportionation may be a problem with other alkyl halides, particularly with secondary or tertiary halides. This reaction is probably catalyzed by minor amounts of heavy metal halides and may very well result from impurities in the magnesium. In the authors' experience, at least, satisfactory yields have usually been obtained by using Dow's pure magnesium turnings with primary and secondary alkyl chlorides, primary alkyl bromides, and aryl bromides. Certain secondary and tertiary halides might react more satisfactorily if a purer magnesium were used. No difficulties have been encountered in the use of mild steel reactors for the manufacture of Grignard reagents.

The presence of moisture or alcohol in commercial or recovered ether leads to the formation of the parent hydrocarbon by the reaction:

$$RMgX + HOR \rightarrow RH + Mg(OR)X \qquad (7)$$

In most cases this inhibits the starting of the reaction, possibly because the insoluble gelatinous Mg(OH)X [or Mg(OR)X] coats the magnesium and prevents contact with the halide. A further, minor problem is introduced when the hydrocarbon formed is noncondensable. In that case the hydrocarbon must be vented from the system to prevent excessive build-up of pressure and hence of temperature in the vessel. These problems can often be avoided by treating the ether with a small amount of preformed Grignard reagent.

The reaction of Grignard reagents with oxygen is seldom a problem in commercial operation because the reactor is always purged with nitrogen before ether is introduced and traces of oxygen are usually not appreciably deleterious to the reaction. In some

instances, however, very small traces of oxygen lower the yield in the next step very drastically. Great care is therefore taken to exclude all oxygen when especially sensitive reagents are being prepared.

The question of stability of Grignard reagents on storage sometimes arises. However, reagents which had been stored for as much as 5 years in steel drums or tightly sealed glass bottles had not deteriorated detectably as judged by acid titration, although the reaction indicated in Equation 5 appeared to have reached equilibrium, depositing magnesium chloride from certain Grignard chlorides. Storage at low temperatures may in some cases—e.g., that of phenylmagnesium bromide—cause part of the reagent to crystallize out. Upon warming, the crystals dissolve again with some difficulty.

In general, yields of Grignard reagent in excess of 90% have been obtained in the plant described here.

Reaction with Carbonyl Compounds

The reaction of the Grignard reagent with a carbonyl, or other reactive compound, is carried out in *R*-3. This vessel is essentially a duplicate of *R*-2 with certain added accessories, notably the fractionating column and condenser. In the ordinary case, the Grignard reagent is transferred from *R*-2 to *R*-3 and the carbonyl compound is added to it over a period of time from the feed tank. The temperature is controlled by heating or cooling with the jacket. In some cases much of the ether in the Grignard solution is replaced by a higher boiling solvent such as toluene, in order to maintain a higher reaction temperature at moderate pressure. The replacement is accomplished by adding toluene slowly, while distilling ether through the column and condenser. When this is done some residual ether, which appears to be tightly held by the reagent, will be freed by the addition of the carbonyl compound and must be allowed to distill out.

The reverse addition—that is, the addition of Grignard reagent to the carbonyl compound dissolved in ether—can be carried out in the same equipment if it is required. In that case the Grignard solution is transferred slowly from *R*-2 into *R*-3 which contains the carbonyl compound in solution.

In either case, after the reaction is complete, it is usually convenient to replace the ether with toluene, distilling and condensing the ether and collecting it in the ether storage tank. This dry ether is used in subsequent preparations of Grignard reagent. An excess of carbonyl compound, if it is very volatile, must be avoided if ether is reclaimed in this way, however.

Replacement of ether with toluene often introduces a further complication, in that many of the magnesium complexes of the reaction products are insoluble in hydrocarbons and may set up into nearly solid masses which are virtually impossible to remove from the vessel. A considerable amount of balancing of factors is therefore necessary in this stage of the operation.

Hydrolysis of Complex

The magnesium complex which results from the reaction of the Grignard reagent with carbonyl compounds is hydrolyzed with dilute acid in *R*-4. This vessel is charged with the required amount of sulfuric acid, water, and ice, and the mixture from *R*-3 is pumped in rapidly while vigorous agitation is maintained to assure intimate contact between complex and acid. The temperature is adjusted by the proportions of ice and acid so that the final temperature after hydrolysis approximates 0°C. Under these conditions it has been possible to use a mild steel vessel for the hydrolysis without encountering excessive corrosion.

After the hydrolysis is complete, the aqueous layer is drawn off and the organic layer is washed with suitable aqueous solutions to remove acid and other undesirable impurities which vary with the particular materials involved. Where especially acid-

sensitive products are encountered, the hydrolysis may be carried out with an excess of ammonium chloride instead of sulfuric acid.

Most of the materials which have been made in the plant described here are nonvolatile and water-insoluble. Therefore the organic layer which contains the hydrolyzed product is finally transferred to *R*-5, where it is steam-stripped to remove solvents. The product is separated from the water by simple decantation if it is a liquid or by filtration if it is a solid. Further purification by conventional means is carried out where it is required.

Other Reactions

A wide variety of other Grignard reactions can be carried out in this same equipment. Metathetical reactions with halides, both organic and inorganic, as well as reactions with compounds which contain double or triple bonds are readily handled. A number of compounds which contain active hydrogens react with Grignard reagents to form new reagents of the Grignard type. A particularly useful example is the Ivanov reaction (*9*), in which the alpha hydrogen of sodium phenyl acetate is replaced by MgX:

$$C_6H_5CH_2COONa + RMgX \rightarrow C_6H_5\underset{\displaystyle MgX}{\underset{|}{C}}HCOONa \qquad (8)$$

This compound reacts with carbonyl compounds in the normal fashion, to produce β-hydroxy or unsaturated acids.

Although it has not been done in this plant, organocadmium compounds (*5*) can be formed by reaction with Grignard reagents, allowing the preparation of ketones from acid chlorides to be carried out.

$$2RMgX + CdCl_2 \rightarrow R_2Cd + 2MgXCl \qquad (9)$$

$$R_2Cd + 2R'COCl \rightarrow 2RCOR' + CdCl_2 \qquad (10)$$

From the standpoint of custom Grignard synthesis, the plant described here accomplishes the major objective of carrying out all of the reaction steps which require the use of ethyl ether. The customer thus avoids the major problem of the Grignard synthesis—the hazards of handling ethyl ether.

The plant is housed in a somewhat isolated steel building, wired throughout with explosion-proof, Class I, Group D or Class II, Group G fixtures and motors. It is equipped for both general forced ventilation and spot ventilation at points of greatest hazard. No serious accidents have occurred in the operation of this plant.

Other Grignard Processes

Several other procedures for producing Grignard reagents should be mentioned. One, often referred to as a "cyclic reactor," has been described by Rowlands, Greenlee, and Boord (*14*). Its purpose is to make possible the preparation of Grignard reagents from highly reactive halides which have a predilection for the Wurtz reaction. Because high dilution favors the Grignard reaction, ether is distilled from a flask, condensed, and allowed to flow back through a column packed with amalgamated magnesium. The halide is introduced very slowly into the returning condensate at the top of the column. In this way, it is reported, very high yields of Grignard reagents derived from highly active halides of the allyl and benzyl types are obtained. Commercial utilization of this process has not, however, been reported.

A process has been patented (*8, 17, 18, 21*) which utilizes the highly activated condition of freshly cut magnesium to bring about the formation of Grignard reagents from aryl chlorides. According to the patents, a solution of an aryl chloride in ethyl ether or in a dialkyl ether of ethylene glycol, is allowed to flow through a chamber surrounding a rotating cutting head while the latter shaves chips from a pure mag-

nesium billet. The process is said to produce high yields of arylmagnesium chlorides which are difficult to obtain by other means. How far this process has been commercialized is not known to the authors, although it is known that several machines have been used in pilot operations.

Arylmagnesium chlorides have also been reported (*3, 19, 20, 23*) to result from the so-called "solventless" reaction of aryl chlorides with magnesium. In point of fact these processes have usually employed an excess of the halide as solvent and the reported yields have not always been very attractive. The reaction is usually carried out under pressure at elevated temperatures. Commercial use of this procedure has been made (*2*).

Buc (*4*) has patented a process for preparing Grignard reagents by continuously feeding an organic halide into a reaction zone containing magnesium turnings and continuously removing the reagents as it is formed. It is not known whether this process has ever been placed in commercial operation.

Advantages and Disadvantages of the Grignard Reaction

Many of the reactions of Grignard reagents can be or have been carried out through the use of other organometallic compounds. The reactions of sodium, lithium, zinc, and cadmium alkyls, for example, have been studied in detail. The Grignard reagents have, however, been much more widely used in organic synthesis than have any of the others.

Perhaps the first reason for their success is that Grignard reagents utilize the readily available and easily handled magnesium. Magnesium turnings are suitable for use as received and can be stored for long periods without deterioration. Furthermore, magnesium does not present major hazards in handling or disposal of wastes nor are its compounds generally considered to be toxic. Its price is not exorbitant.

The Grignard reagents themselves are easily prepared in simple equipment. They are stable in storage and are not generally spontaneously flammable in contact with air or moisture. Methylmagnesium bromide in $4M$ strength has, however, been observed to ignite spontaneously with water and perhaps other Grignard reagents might do so under certain circumstances. Further advantages of Grignard reagents are that they are marketed commercially and that, for those who wish to avoid entirely the hazards of handling ethyl ether, custom manufacturing facilities are available.

Finally the reactions of Grignard reagents have been so thoroughly studied that their course can be accurately predicted in most cases. Many of their reactions proceed in a clean-cut fashion to provide good yields of the desired product. Indeed, for these reasons Grignard reactions have been widely employed in the establishment of the structures of new compounds.

The hazards involved in the handling of ethyl ether cannot be ignored; in fact, the problems of the Grignard reaction are largely the problems of handling ethyl ether with safety.

The unreactivity of certain chlorides, which forces one to use the corresponding bromides, is a serious disadvantage of the Grignard process, as is the sensitivity of many of the more reactive halides to the Wurtz and disproportionation reactions. It is also unfortunate that Grignard reagents usually do not produce ketones by reaction with acid chlorides or anhydrides. The ready conversion of Grignard reagents to organocadmium compounds (*5*), however, makes it possible to prepare ketones in excellent yield from acid chlorides. Reaction of Grignard reagents with nitriles likewise frequently gives poor results and reductive side reactions interfere in some reactions with carbonyl compounds. These reductions appear to be especially important in reactions with ketones, less so with aldehydes and esters.

The Grignard reaction often provides the best method for producing a wide variety of compounds. Its industrial importance is increasing as the demand for more intricate and specialized compounds grows.

Economic Factors

It is possible here to make only broad generalizations regarding the economics of the Grignard reaction.

A consideration of one of the more useful Grignard reactions, the reaction with carboxylic esters, will serve to illustrate a number of the economic factors which enter into Grignard reactions.

$$2RMgX + R\overset{O}{\overset{/\!/}{C}}OR' \rightarrow R_3COH + 2Mg(OH)X \qquad (11)$$

For each pound mole of useful product obtained, 2 pound moles of basic magnesium halide are formed. Unless the operation is very large, it is not economical to recover this material, but it contains magnesium worth about $25, and, in reactions where the bromide is required, $40 worth of bromine. It is immediately seen that chlorides would be much more economical than bromides, in the Grignard reaction. Furthermore, ketones, which require only 1 mole of Grignard reagent, will appear to be preferred over esters, which require 2 moles, for producing tertiary alcohols. Some of this advantage of ketones is often lost, however, by side reactions, and in many instances the desired ketone is not readily available.

It may be concluded that few compounds can be produced by this reaction for a raw material cost of less than $1.00 per pound. Therefore, the commercial use of the Grignard reaction is practically restricted to the manufacture of relatively expensive materials, such as perfumes, pharmaceuticals, silicones, and even certain agricultural chemicals. In general, then, where great specificity of structure is a controlling factor, many products may be made most economically by the Grignard reaction.

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Preparation of Alkyl Mercurials with Tetraethyllead

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The inexpensive preparation of alkyl mercurials by a unique method using tetraethyllead is described. The commercial methods of preparation of some useful ones and the health hazards involved are given. The properties, utilization as fungicides and seed disinfectants, and effect on agriculture of alkyl mercurials are discussed.

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In 1923 methylmercuric iodide was found by Gassner and Esdorn (*5*) to be a powerful fungicide. Klages (*9*) extended these findings to a series of alkylmercuric halides, showing them to be 25 times as efficient as mercuric chloride. Tisdale and Cannon (*14*) showed by extensive tests that the alkyl mercurials are effective seed disinfectants for the control of fungicidal diseases.

Alkylmercuric halides of the type RHgX were well known, but their method of preparation, such as the reaction of diethylzinc and mercuric chloride (*12*), was difficult and inefficient. Therefore, the products were much too expensive for use as fungicides. A method was needed to produce these potentially valuable compounds at a reasonable cost for widespread application.

In 1930, a method for the preparation of alkyl mercury compounds was patented by Kharasch (*7*), which comprised heating mercury salts with an alkyl derivative of quadrivalent lead, more particularly tetraethyllead. This provided the necessary economical method for their commercial use.

The reaction is a general one and may be shown as follows:

$$R_4Pb + 2Hg^{++} \rightarrow 2RHg^{+} + R_2Pb^{++} \qquad (1)$$

Preparation

By utilizing this method, the following typical, commercially important alkyl mercurials may be prepared.

Ethylmercuric Chloride. This was the first compound produced for commercial use (*8*). In the reaction of mercuric chloride with tetraethyllead, the latter acts as a transalkylation agent:

$$2HgCl_2 + Pb(C_2H_5)_4 \rightarrow (C_2H_5)_2PbCl_2 + 2C_2H_5HgCl \qquad (2)$$

The reaction may be carried out conveniently in the laboratory.

Tetraethyllead dissolved in ethyl alcohol is added gradually to a suspension of mercuric chloride in ethyl alcohol. After heating at 65°C. for 4 hours, the hot reac-

tion mass is clarified by filtration. The precipitate of ethylmercuric chloride, which separates on cooling, is filtered off and recrystallized from ethyl alcohol. The yield of ethylmercuric chloride is 72% of theory from mercuric chloride.

In commercial practice, the mercuric chloride is ball-milled with an inert ingredient such as talc, and the tetraethyllead is added at intervals while milling is carried out in a brick-lined mill with porcelain balls. Care is taken to prevent undue temperature rise. The reaction is carried out essentially in dry form, and further inert diluent is added so that the final mass has an ethylmercuric chloride content of 2.0%. It is utilized as such.

The great value of this method of preparation lies in the mild conditions employed and in the type of equipment used which allows manufacture of large batches requiring little processing.

Ethylmercuric chloride, though a very efficient fungicide, had a deficiency; it showed instability with evolution of diethylmercury, a highly volatile compound which is very toxic to humans. A study of the reaction suggested that one of the following secondary reactions might take place which would explain the formation of diethylmercury:

$$RHgCl + R_3PbCl \rightarrow R_2Hg + R_2PbCl_2 \quad (3)$$

$$R_4Pb + 2RHgCl \rightarrow RPbCl_2 + 2R_2Hg \quad (4)$$

Various experiments were unsuccessful in determining if the secondary reactions were taking place. Because it is possible to obtain high yields of ethylmercuric chloride, the more probable explanation of the formation of diethylmercury is that it comes from a disproportionation equilibrium with ethylmercuric chloride (*6*). This may come about in the following manner:

$$2C_2H_5HgCl \leftrightarrows (C_2H_5)_2Hg + HgCl_2 \quad (5)$$

The evolution of diethylmercury can be eliminated by the use of bis(ethylmercuric) phosphate, a much more stable compound.

Bis(ethylmercuric) Phosphate. This compound is prepared (*3*) by the interaction of mercuric oxide, phosphoric acid, and tetraethyllead. The tetraethyllead acts as a transalkylation agent. The following reactions occur, but the steps are carried out simultaneously:

$$2HgO + 2H_3PO_4 \rightarrow 2HgHPO_4 + 2H_2O \quad (6)$$

$$2HgHPO_4 + (C_2H_5)_4Pb \rightarrow (C_2H_5Hg)_2HPO_4 + (C_2H_5)_2PbHPO_4 \quad (7)$$

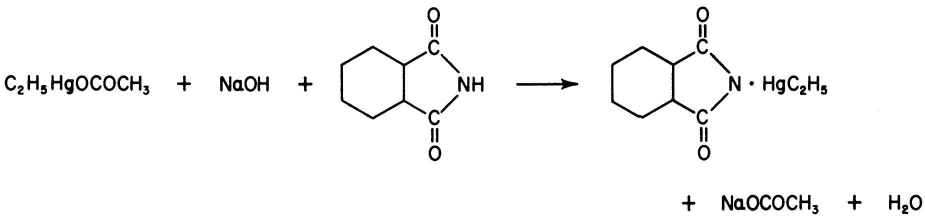
The system is highly exothermic, the heat evolved being 26 kcal. per mole of mercuric oxide. In commercial processes, the reaction is carried out most conveniently in the solid state by the method for preparing ethylmercuric chloride. The time of milling varies with the apparatus used and may be as long as 18 hours. After the reaction is completed, the reaction mass is diluted further with an inert ingredient to 5.0% bis(ethylmercuric) phosphate. It is sold as such.

Ethylmercuric Acetate. Ethylmercuric acetate (*10*), originally prepared by heating diethylmercury with acetic acid, is prepared readily by the reaction of mercuric acetate with tetraethyllead:

$$3Hg(OCOCH_3)_2 + (C_2H_5)_4Pb \rightarrow 3C_2H_5HgOCOCH_3 + C_2H_5Pb(OCOCH_3)_3 \quad (8)$$

It is water-soluble and may be separated readily from ethyllead triacetate.

It is utilized as a water-soluble fungicide and is a convenient starting material for the preparation of a series of alkyl mercurials. Ethylmercuric acetate will condense readily, in an alkaline medium, with compounds having a replaceable hydrogen atom. The reaction is a general one—for example, ethylmercuric acetate condenses with phthalimide to form *N*-ethylmercuriphthalimide:



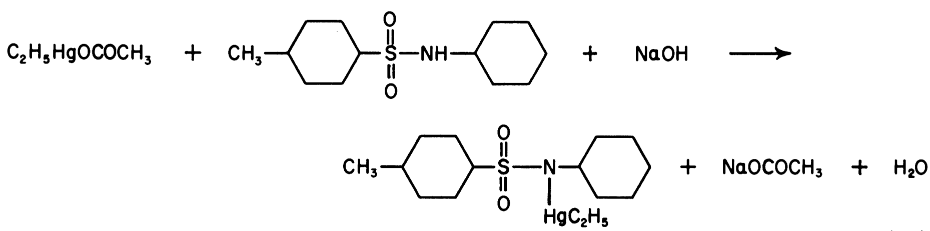
(9)

Ethylmercuric acetate reacts in a similar manner to replace hydrogen of mercaptans, phenols, and compounds which enolize, such as the 1,3-diketones.

An example of the use of ethylmercuric acetate is the preparation of *N*-ethylmercuri-*p*-toluenesulfonanilide.

***N*-Ethylmercuri-*p*-toluenesulfonanilide.** The preparation of *N*-ethylmercuri-*p*-toluenesulfonanilide from mercuric acetate, tetraethyllead, and *p*-toluenesulfonanilide is described by Mowery (*11*):

$$3Hg(OCOCH_3)_2 + (C_2H_5)_4Pb \rightarrow 3C_2H_5HgOCOCH_3 + C_2H_5Pb(OCOCH_3)_3 \quad (10)$$



(11)

Mercuric oxide is dissolved in glacial acetic acid at 95°C., and the mercuric acetate formed reacts with tetraethyllead at the same temperature. After cooling, the solution is added to a mixture of sodium hydroxide and ice, and to this is added a solution made by dissolving *p*-toluenesulfonanilide in aqueous sodium hydroxide. After stirring at room temperature, the precipitate is filtered off and washed free of alkali with water. After drying, a 94% yield of *N*-ethylmercuri-*p*-toluenesulfonanilide of 90% purity, as based on the mercury content, is obtained. This material, after dilution with talc to a 7.70% concentration, is sold as Ceresan M seed disinfectant (E. I. du Pont de Nemours & Co.).

Properties of Alkyl Mercurials

Ethylmercuric chloride, bis(ethylmercuric) phosphate and *N*-ethylmercuri-*p*-toluenesulfonanilide all exhibit volatility. Bis(ethylmercuric) phosphate is less volatile than ethylmercuric chloride, while *N*-ethylmercuri-*p*-toluenesulfonanilide is still less volatile. Ethylmercuric chloride has a low vapor pressure, sublimes readily into air at 40°C., and has a melting point of 195°C. It can be steam distilled. It tends to evolve diethylmercury, and in contact with water vapor and organic materials this reaction is accelerated.

All alkyl mercurials are powerful fungicides. Ethylmercuric chloride is about 25 times more powerful than mercuric chloride as a fungicide (*5*). In compounds of the type C_2H_5HgX, the X part of the molecule has small effect on the fungicidal activity of the compound based on the mercury content, but the solubility characteristics, vesicant action, and toxicity to human beings are largely controlled by X.

Health Control

The hazards associated with the manufacture of alkyl mercury compounds are well known (*1*). They are potent skin irritants, and will produce severe vesiculation and burns on brief skin contact. In addition, these organic mercurials are absorbed through the skin as well as the lungs, producing systemic, acute, and chronic mercury poisoning (mercurialism). At present, most codes designate a maximum allowable concentration of mercury in the atmosphere for an 8-hour day at 0.1 mg. per cubic meter (*4*).

Disabilities resulting from excess mercury absorption can be prevented. The prevention is one of adequate safety and health measures in the manufacture of these organic mercurials. Adequate ventilation is mandatory in operating buildings, and the mercury content in air is determined continuously.

A program to maintain the normal health of persons exposed to the alkyl mercurials has been effective. Workers are required to wear protective clothing that constitutes an effective barrier to skin absorption to these organomercurials. A monthly general physical examination which includes complete urinalysis and blood count is performed. Urinary mercury levels of operating personnel are checked before assignment to this process. If the urinary level climbs to 0.05 mg. of mercury per liter, weekly analyses are made until the level drops below 0.05 mg. If the level continues to climb and eventually reaches 0.1 mg. per liter, the man is removed completely from contact with organic mercurials until the mercury concentration drops below 0.1 mg. per liter (*4*).

On following this program, no clinical indications of mercurialism have occurred. The present maximum allowable concentration of 0.1 mg. per cubic meter of air for the organic mercurials (or 0.08 mg. per cubic meter of air based on elemental mercury) appears realistic. From the adequacy of health preservation experience of 6 years under this program, the practicality of reduction of this level should be examined carefully.

Utilization as Fungicides

The use of alkyl mercurials has been chiefly as disinfectants for seeds and grains and for protection of newly sawed wood from fungus attack, particularly in humid climates (*13*).

Commercialization of the alkyl mercurials as fungicides required a reliable testing method to show conclusively that they were efficient. The original test method was based on the volatile nature of the compounds. The mercurial was placed below the seeds or grains in a closed container, though not in contact with them or their supporting medium. On germination, the stand of seedlings was compared to a stand grown without treatment. Extensive testing was carried out under varying conditions against various fungicidal diseases, such as bunt or stinking smut, seed rots, and blights of cereal grains (*14*). Protection against numerous fungicidal diseases was given by the alkyl mercurials, in that more seedlings and healthier seedlings were obtained.

To secure maximum efficiency as a fungicide, the product must be in its most suitable physical form and one which allows easy application. In the early development, a finely divided product diluted with inert solid materials (*3*), such as talc or calcium carbonate, was utilized as a dry powder. It is more feasible to apply it to seeds and grains by a wet method and thus eliminate the dust nuisance. The present trend is to utilize alkyl mercurials from aqueous media, either as slurries or as water-soluble compounds. The newly developed *N*-ethylmercuri-*p*-toluenesulfonanilide was formulated to be applied from a water slurry, and as Ceresan M seed disinfectant it is used more extensively now than ethylmercuric chloride and bis(ethylmercuric) phosphate. It is particularly useful for the control of bunt or stinking smut,

seed rot, and seedling blights in grains, and for the control of seed-borne fungus and bacterial diseases which cause seed rot in cotton. One gram of *N*-ethylmercuri-*p*-toluenesulfonanilide is ample to kill all the spores in 1 bushel of wheat, which is a ratio of 1 to 27,000 or 0.0033%.

Other Mercurials. A number of alkyl and aryl mercurials, prepared by methods other than by the use of tetraethyllead, are utilized as fungicides (*10*). They fall mainly into four types: acetates, such as 2-methoxyethylmercuric acetate, phenylmercuric acetate, and the ammonia complex of phenylmercuric acetate; ureas, such as phenylmercuriurea and (acetoxymercuri)methylurea; phenols, such as (hydroxymercuri)nitrophenol and (hydroxymercuri)chlorophenol, and phenylmercuric salicylate; and others, such as methylmercuricyanoguanidine.

Effect on Agriculture. The use of alkyl mercurials is widespread for the control of fungicidal diseases, especially those of wheat and cereal grains. It has made possible increased yields of wheat, corn, cotton, and other vital crops. Approximately 35% of the seed utilized in these crops is treated with a fungicide, and of this about 30% is treated with an alkyl mercurial. The actual saving by the use of a fungicide is difficult to determine, but a 10% yield increase is to be expected, or for each $1 spent on the purchase of fungicides $20 is returned. The estimated over-all yearly value of the alkyl mercurials is of the order of $100,000,000, and they have contributed measurably to our agricultural abundance.

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Organoboron Compounds

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In this paper the definition of organoboron compounds is limited to those containing boron-carbon bonds. The nomenclature is that proposed by Wartik and Schaeffer and the Organic Subcommittee on Boron Nomenclature (*116, 159*).

Preparations

Trialkylboranes or Triarylboranes. The first report of the preparation of boron-carbon bonds was made by Frankland almost one hundred years ago. Triethylborane was prepared by the reaction of diethyl zinc with ethyl borate.

$$3(C_2H_5)_2Zn + 2B(OC_2H_5)_3 \rightarrow 2(C_2H_5)_3B + 3Zn(OC_2H_5)_2$$

As a result, the alkylboranes are sometimes referred to as Frankland reagents by European writers (*52*). Many alkyl- and arylboranes have been prepared by similar methods using alkoxy- or haloboranes as the boron source, an alkyl or aryl halide as the carbon source, and an active metal as the condensing agent.

$$BY_3 + 6M + 3RX \rightarrow BR_3 + 3MY + 3MX$$

Y = halide, oxide or alkoxide; X = halide; M = Li, Na, Mg, Zn, or Al; R is alkyl or aryl.

In most cases the intermediate metal alkyl or alkyl metal halide was isolated. In the first preparations of arylboranes, diarylmercury compounds were used (*16, 37, 69, 77–80, 82, 83, 99, 106, 107, 148, 162*). In the case of hydrocarbons which react with active metals, the hydrocarbon has sometimes been used as the carbon source—e.g., naphthalene (*88*). Ethylene has also been used as the carbon source in forming an intermediate alkylaluminum halide (*124*).

$$Al + AlCl_3 + C_2H_4 \rightarrow C_2H_5AlCl_2 + (C_2H_5)_2AlCl$$

The preparation of a boron-carbon bond directly from a boron compound and a hydrocarbon was first reported by Pace. Attempts to reproduce this preparation have been unsuccessful (*113*). Arnold has patented the reaction of acetylene with trichloroborane in the presence of mercurous chloride to form chlorovinylborane (*2*).

$$BCl_3 + C_2H_2 \xrightarrow{Hg_2Cl_2} Cl{-}CH{=}CH{-}BCl_2$$

The ease of elimination of acetylene, by these compounds, in the presence of bases limits their usefulness (*12*).

$$Cl{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}BCl_2 + 3OH^- \rightarrow B(OH)_3 + C_2H_2 + 3Cl^-$$

Hurd has reported the preparation of triethylborane from ethylene and diborane. The kinetics of this reaction was studied by Whatley and Pease (*64, 161*).

$$B_2H_6 + 6C_2H_4 \rightarrow 2(C_2H_5)_3B$$

Others have studied the reaction of diborane with unsaturated organic compounds, but the products are usually polymeric (*114, 147, 149*).

Schlesinger found that the reaction of diborane with metal alkyls generally gave metal borohydrides and alkyl boranes (*141*)—e.g.,

$$(CH_3)_3Al + 2B_2H_6 \rightarrow Al(BH_4)_3 + (CH_3)_3B$$

Brokaw and Pease found triethylborane among the products of the reaction of aluminum borohydride with ethylene.

$$Al(BH_4)_3 + 12C_2H_4 \rightarrow Al(C_2H_5)_3 + 3(C_2H_5)_3B$$

Mono- or Dialkylboranes or Mono- or Diarylboranes. In general, the preceding preparations can be modified to give chiefly mono- or dialkylboranes by proper reactant stoichiometry (*167*).

$$BY_3 + 6M + RX \rightarrow BRY_2 + MY + MX$$

Wiberg and Fischer have also found that mono- or dialkylboranes may be prepared by the redistribution of trialkylboranes with halo- or alkoxyboranes (*45–48, 162*).

$$BR_3 + BX_3 + B(OR) \underset{<100^\circ\ C.}{\overset{>100^\circ\ C.}{\rightleftharpoons}} 3BR(X)OR$$

Such redistributions occur only at elevated temperatures. At room temperatures the mixed products tend to disproportionate to the symmetrical boranes.

Tri-*p*-tolylborane was exchanged with tribromoboranes on standing at room temperature for 5 days. Only *p*-tolylbromoboranes resulted. The reaction was much more rapid than the exchange reaction of triphenylborane with tribromoborane (*158*).

$$(H_3C—C_6H_4)_3B + BBr_3 \rightarrow H_3C—C_6H_4BBr_2 + (H_3CC_6H_4)_2BBr$$

The only reported preparation of a mixed trialkylborane was by Kraus from dibutylboryl sodium and methyl iodide (*6*).

$$(C_4H_9)_2BNa + CH_3I \rightarrow (C_4H_9)_2BCH_3 + NaI$$

Letsinger was able to prepare phenyl(1-naphthyl)hydroxyborane by the reaction of a 1-naphthyldialkoxyborane with phenyllithium.

$$C_6H_5Li + (1—C_{10}H_7)B(OR)_2 \rightarrow LiC_6H_5(1—C_{10}H_7)B(OR)_2$$

$$\downarrow HOH$$

$$LiOH + 2ROH + C_6H_5(1—C_{10}H_7)BOH$$

Attempts to prepare mixed alkylarylboranes were unsuccessful (*88*).

The dialkylhaloboranes can be prepared by reaction of the trialkylborane with a hydrogen halide.

$$(CH_3)_3B + HCl \rightarrow (CH_3)_2BCl + CH_4$$

The addition of aluminum halide and increased temperatures result in the removal of a second molecule of the alkane (*11, 52, 143, 162*).

$$(CH_3)_2BCl + HCl \xrightarrow{AlCl_3} CH_3BCl_2 + CH_4$$

Long has reported the preparation of dipropyliodoborane from tripropylborane and iodine at 140°C.

$$(C_3H_7)_3B + I_2 \rightarrow (C_3H_7)_2BI + B_3H_7I$$

The iodine may be replaced by chlorine or bromine by reaction with the appropriate antimony halide (*95*).

$$3(C_3H_7)_2BI + SbCl_3 \rightarrow 3(C_3H_7)_2BCl + SbI_3$$

The alkyl fluoroboranes were first prepared by Burg from trifluoroborane and the anhydride of the corresponding hydroxyborane (*20*).

$$(CH_3BO)_3 + 3BF_3 \rightarrow CH_3BF_2 + (FBO)_3$$

$$3(CH_3)_2BOB(CH_3)_2 + 3BF_3 \rightarrow 6(CH_3)_2BF + (FBO)_3$$

McCusker found that Burg's method was generally satisfactory for preparing the alkyldifluoroboranes and that they were stable to disproportionation. The secondary and tertiary compounds were spontaneously flammable. The trialkylboroxins and aluminum chloride gave evidence of the formation of alkyldichloroboranes (*98*).

Alkylalkoxyboranes. The monoalkyldialkoxyboranes may be prepared by the slow oxidation of alkyl boranes (*52*)

$$R_3B + O_2 \rightarrow RB(OR)_2$$

or by the alcoholysis of the monoalkylhaloboranes or the monoalkyldiboranes.

$$CH_3BCl_2 + 2HOC_2H_5 \rightarrow CH_3B(OC_2H_5)_2 + 2HCl$$

$$CH_3B_2H_5 + 5HOC_2H_5 \rightarrow CH_3B(OC_2H_5)_2 + B(OC_2H_5)_3 + 5H_2$$

The monoalkyldialkoxyboranes are evidently intermediates in the reactions of the metal alkyls with excess trialkoxyborane, but they have seldom been isolated (*146*).

With moist air the trialkylboranes are reported to yield dialkylalkoxyboranes (*67*).

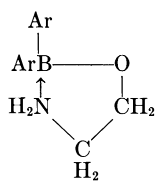
$$(C_4H_9)_3B + O_2 \xrightarrow{\text{moisture}} (C_4H_9)_2BOC_4H_9$$

Di-*n*-butoxyphenylborane reacted with phosphorus pentachloride to give phenyl dichloroborane. Similar reactions were obtained with both *m*- and *p*- bis-(dibutoxy boryl)benzenes. Attempts to reduce the phenyldichloroboranes with lithium aluminum hydride did not give phenylborane. Phenyldifluoroborane was prepared by the reaction of dimethoxyphenylborane with trifluoroborane (*99*).

$$C_6H_5B(OC_4H_9)_2 + PCl_5 \rightarrow C_6H_5BCl_2 + (C_4H_9O)_2PCl_3?$$

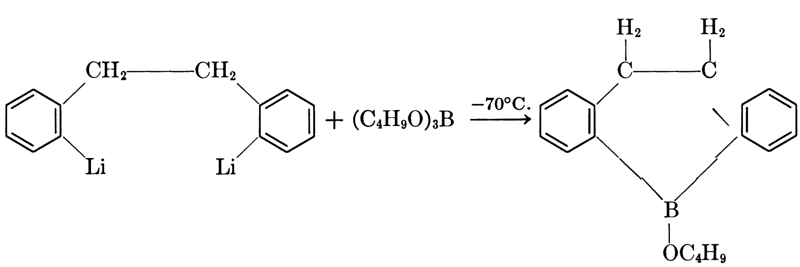
$$3C_6H_5B(OCH_3)_2 + 2BF_3 \rightarrow 3C_6H_5BF_2 + 2B(OCH_3)_3$$

Letsinger has prepared a number of diarylaminoethoxyboranes and found them to be unusually stable because of the internal dative bond

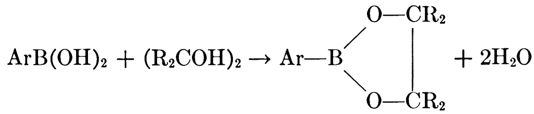


He found these compounds convenient for isolating diarylhydroxyboranes, and the diethanolamine derivatives for the isolation of the aryldihydroxyboranes (*90*).

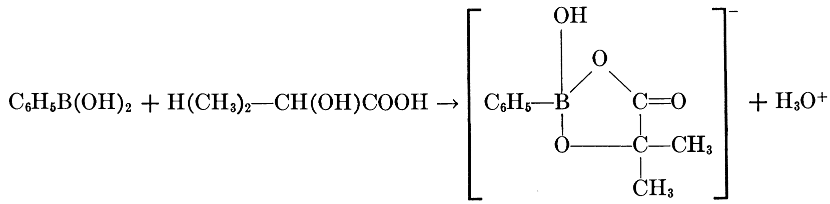
He also reported the isolation of the first reported heterocyclic compound with only carbon and boron in the ring, by the following reaction (*91*):



Kuivila has investigated the ethers of phenyldihydroxyborane with several polyalcohols, including sorbitol, mannitol, pinacol, catechol, pentaerythritol, diethyl D-tartrate, and *cis*-indan-1,2-diol. These were precipitated by merely adding the phenyldihydroxyborane to a saturated solution of the polyol (*86*).



He also found that α-hydroxyisobutyric acid ties up phenyldihydroxyborane as a complex anion (*84*).



Recent work by Letsinger has demonstrated that the dialkylalkoxyboranes may be prepared from Grignard reagents and alkoxyboranes by the use of 1,2-ethandiol to separate the dialkyl from the monoalkylated product. The resulting ethers differ widely in volatility (*89*).

$$2(C_4H_9)_2BOCH_3 + HOCH_2CH_2OH \rightarrow (C_4H_9)_2BOCH_2CH_2OB(C_4H_9)_2 + 2CH_3OH$$

$$C_4H_9B(OCH_3)_2 + HOCH_2CH_2OH \rightarrow C_4H_9B(OCH_2^-)_2 + 2CH_3OH$$

Meerwein found in an unusual reaction that trialkylboranes reacted with aldehydes to give dialkylalkoxyboranes (*102*).

$$(C_2H_5)_3B + C_6H_5CHO \rightarrow (C_2H_5)_2BOCH_2C_6H_5 + C_2H_4$$

Boron bonds to most elements other than carbon hydrolyze to form the hydroxyboranes (*41, 43, 70, 134, 139, 142*).

$$R_2BY + HOH \rightarrow R_2BOH + HY$$

R = alkyl or aryl, Y = halogen, alkoxide, hydride, amide, or oxide.

The alkylhydroxyboranes lose water readily (*43*).

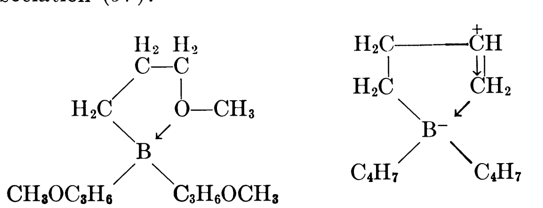
$$2R_2BOH \rightarrow HOH + R_2BOBR_2$$

$$3RB(OH)_2 \rightarrow \underset{\text{cyclic}}{(RBO)_3} + 3H_2O$$

The trialkylboroxins can also be prepared from boric oxide and the trialkylborane (*58*).

$$B_2O_3 + (CH_3)_3B \rightleftharpoons (CH_3)_3B_3O_3$$

Alkylboranes with Functional Groups in the Side Chain. Lyle has studied the preparation of trialkyl boranes with terminal or alpha double bonds or ethereal groups in the side chain. He found that the stability of the Grignard reagent was generally limiting in these preparations. Physical properties and infrared spectra gave evidence of intramolecular association (*97*).



Rothstein and Saville obtained bis(diallylboryl) oxide and tri-*n*-butylborane rather than the expected allyldi-*n*-butylborane from the reaction of allylmagnesium bromide with di-*n*-butylbromoborane. The evident course of the reaction was

$$2C_3H_5MgBr + 3(C_4H_9)_2BBr \rightarrow 2(C_4H_9)_3B + (C_3H_5)_2BBr + 2MgBr_2$$

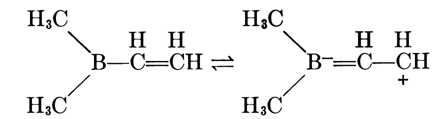
$$2(C_3H_5)_2BBr + HOH \rightarrow 2HBr + (C_3H_5)_2BOB(C_3H_5)_2$$

Bis(diallylboryl) oxide was also obtained from the reaction of allylmagnesium bromide with trifluoroborane (*123*).

Ritter has prepared several vinyl-type boranes by the reaction of vinylsodium or propenyllithium with dimethylbromoborane.

$$CH_2{=}CHNa + (CH_3)_2BBr \rightarrow (CH_3)_2BCH{=}CH_2 + NaBr$$

The products were unusually stable to disproportionation, apparently because of pi bonding between the vinyl group and the boron



Methyldivinyl, trivinyl, and trimethylboranes were obtained as well as the unusual bis(dimethylboryl)ethane, probably from ethenyldisodium, which is known to be an impurity in vinylsodium preparations (*115*).

$$2(CH_3)_2BBr + NaCH{=}CHNa \rightarrow 2NaBr + (CH_3)_2BCH{=}CHB(CH_3)_2$$

Diborylalkanes and Diborylbenzenes. Schlesinger prepared bis(dichloroboryl)-ethane by the reaction of diboron tetrachloride with ethylene

$$B_2Cl_4 + C_2H_4 \rightarrow Cl_2BCH_2CH_2BCl_2$$

The chlorines may be replaced by methoxy groups by treatment with methanol and by methyl groups by treatment with dimethyl zinc.

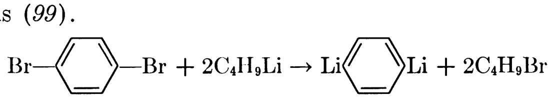
$$Cl_2BCH_2CH_2BCl_2 + 4CH_3OH \rightarrow (CH_3O)_2BCH_2CH_2B(OCH_3)_2 + 4HCl$$

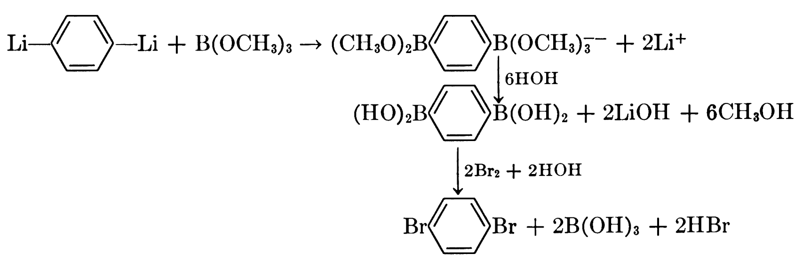
$$Cl_2BCH_2CH_2BCl_2 + 2(CH_3)_2Zn \rightarrow 2ZnCl_2 + (CH_3)_2BCH_2CH_2B(CH_3)_2$$

The methyl derivative decomposes slowly to give trimethylborane and unidentified by-products. Similar products have been prepared by the reaction of diboron tetrachloride with propene, 2-butene, cyclopropane, and acetylene (*154*).

The replacement of the chlorines by hydrogen has not given a stable product (*131*).

McEwen has also prepared the *m*- and *p*-bisdihydroxyboryl benzenes from the corresponding dibromobenzenes. The dilithiumbenzenes were prepared by exchange with butyllithium. The lithium compound was then treated with methyl borate. A similar preparation was carried out using Grignard procedures. The structure of each compound was proved by cleavage with bromine to the respective dibromobenzene and boric acid. These compounds were also prepared from the intermediate bromophenyl boroxins (*99*).





Alkyldiboranes. Trimethylborane and diborane react in proportions of 5 to 1 to give 40% of methyldiborane and 60% of dimethyldiborane. In a 1 to 4 ratio the products are trimethyldiborane and tetramethyldiborane, exclusively (*142*).

$$n/3\ (CH_3)_3B + B_2H_6 \rightarrow B_2H_{6(6-n)}(CH_3)_n$$

The ethyl and propyldiboranes were also prepared by Schlesinger from the corresponding trialkylboranes and diboranes. Mono-, di-, tri-, and tetraethyldiboranes and mono- and dipropyldiboranes were isolated (*138*).

Symmetrical dimethyldiborane is prepared by treating methyldiborane with four times its volume of methyl ether at dry ice temperature. The products are methyl ether–borane, which is stable at dry ice temperature, and symmetrical dimethyldiborane.

$$2CH_3HBH_2BH_2 + 2(CH_3)_2O \rightarrow CH_3HBH_2BHCH_3 + 2(CH_3)_2O : BH_3$$

Rosenblum found that tributylborane decomposed on heating to give butene and dibutyldiborane (*122*).

$$2(C_4H_9)_3B \rightarrow 4C_4H_8 + (C_4H_9)_2B_2H_4$$

Reactions

Many of the reactions of the alkyl- and arylboranes have been covered in the preceding sections.

With Hydrogen. The alkylboranes do not react with hydrogen at ordinary temperature and pressure; however, solid pyrolysis products may be formed under extreme conditions (*5*).

With Metals. Krause first reported a reaction between sodium and triphenylborane to give a colored crystalline product, sodium triphenylborate(-1)

$$(C_6H_5)_3B + Na \xrightarrow{\text{ether}} NaB(C_6H_5)_3$$

The product reacted instantly with oxygen. It was titratable with iodine in ether and reacted with alkyl halides and carbon dioxide. The ethereal solution conducted electricity. The sodium could be removed by shaking with mercury. Tri-*p*-tolylborane behaved similarly (*81*).

Bent studied similar reactions with trinaphthylborane and found that a second atom of sodium could be added. He studied the conductivities of the other solutions of both the mono- and disodium complexes (*9, 36*).

$$B(1—C_{10}H_7)_3 + Na \rightarrow NaB(1—C_{10}H_7)_3$$

$$NaB(1—C_{10}H_7)_3 + Na \rightarrow Na_2B(1—C_{19}H_7)_3$$

Chu has studied the magnetic susceptibility and visible spectrum of sodium triphenylborate(-1). He found that it was not paramagnetic and assumed that the anions must be dimeric. Sodium trimesityl borate(-1) was found to have one unpaired electron. Lack of dimerization is apparently due to steric factors. Tris-1(2-methylnaphthyl) borane removed the sodium from sodium trimesityl borate(-1), presumably because of higher electron affinity (*32, 33*).

$$B(C_{11}H_9)_3 + NaB(C_9H_{11})_3 \rightarrow NaB(C_{11}H_{10})_3 + B(C_9H_{11})_3$$

Krause reported that unlike the triarylboranes, the trialkylboranes did not react with metals (*80*). However, Kraus has reported the reaction of dibutylchloroborane in ether with sodium-potassium alloy to give dibutylboryl

$$(C_4H_9)_2BCl + M \rightarrow MCl + (C_4H_9)_2B$$

where M is 1 equivalent of sodium potassium alloy.

In comparison Wiberg found that the reaction of dimethylchloroborane with sodium gave trimethylborane and a polymeric material (*167*).

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Burg found that upon contact with sodium in liquid ammonia at −78°C. tetramethyldiborane is split equally into ammonia-dimethylborane and an unusual salt.

$$(CH_3)_2BH_2B(CH_3)_2 + 2Na + NH_3 \rightarrow (CH_3)_2HB{=}NH_3 + NaBH(CH_3)_2$$

This salt is stable as a white solid in vacuum even at 90°C. It hydrolyzes rapidly and quantitatively to dimethylhydroxyborane, hydrogen, and sodium hydroxide. Trimethylborane is added in liquid ammonia to form a yellow solid which is also stable in vacuum at 100°C. (*23*).

$$Na_2BH(CH_3)_2 + 3HOH \rightarrow 2NaOH + 2H_2 + (CH_3)_2BOH$$

$$Na_2BH(CH_3)_2 + B(CH_3)_3 \rightarrow Na_2BH(CH_3)_2B(CH_3)_3$$

The corresponding potassium salt was prepared by the same methods, but attempts to prepare the lithium salt were unsuccessful. The sodium salt reduces chlorosilane to silane and reacts with aqueous hydrochloric acid to form apparently polymeric sodium dimethylboryl (*30*).

$$Na_2HB(CH_3)_2 + ClSiH_3 \rightarrow NaCl + SiH_4 + [NaB(CH_3)_2]x$$

Sodium dimethylboryl reacted with ammonia to form aminodimethylborane and a highly reducing residue (*25*).

$$NaB(CH_3)_2 + NH_3 \rightarrow (CH_3)_2BNH_2 + NaH?$$

Reactions with Metal Hydrides or Organometallics. Fisher prepared lithium borohydride by the hydrogenation of a lithium hydride–triethylborane adduct at 240°C. under 2000 p.s.i. in cyclohexane (*50*).

$$LiBH(C_2H_5)_3 + 3H_2 \xrightarrow[3000\ \text{p.s.i.}]{240°\text{C.}} LiBH_4 + 3C_2H_6$$

Triethylborane forms a liquid 1 to 1 adduct with sodium hydride which has not been characterized. Lithium hydride dissolves in a diethyl ether solution of trimethylborane and is recovered as lithium hydride upon evaporation of the solution. Evidently a reversibly formed lithium hydride–trimethylborane adduct is responsible (*19*).

$$LiH + B(CH_3)_3 \rightleftharpoons LiBH(CH_3)_3$$

Aluminum hydride in ether and trimethylborane reacted; however, the product could not be freed from the ether (*132*).

Schlesinger found that trimethylborane reacted with lithium aluminum hydride to form lithium methyltrihydroaluminate and dimethylaluminum hydride (*160*).

$$LiAlH_4 + (CH_3)_3B \rightarrow LiAlH_3CH_3 + (CH_3)_2AlH$$

Trimethylborane reacted with uranium borohydride to give methylated derivatives. Methyltrihydroboratotris(tetrahydroborato)uranium is the most volatile known compound of uranium. Tetrakis(monomethyltrihydroborato)uranium was also isolated. These materials reacted with water and hydrogen chloride as follows (*129*):

$$U(BH_4)_3(BH_3CH_3) + 12H_2O \rightarrow U(OH)_4 + 15H_2 + CH_3B(OH)_2 + 3HBO_2$$

$$U(BH_4)_3(BH_3CH_3) + 6HCl \rightarrow UCl_4 + 6H_2 + 3/2\ B_2H_6 + CH_3BCl_2$$

$$U(BH_3CH_3) + 12HCl \rightarrow UCl_4 + 12H_2 + 4CH_3BCl_2$$

Early attempts to react trimethylborane with metal alkyls and aryls failed (*153*). However, Johnson found that tributylborane reacted exothermally with diphenylmagnesium in ether. Separation into two layers occurred. Only one mole of tributylborane reacted with one mole of diphenyl magnesium. Tributylborane reacted exothermally with ethyllithium, but less vigorously with butyllithium and butylmagnesium bromide. Tributylborane did not react with dibutylzinc (*69*).

$$LiC_2H_5 + B(C_4H_9)_3 \rightarrow LiB(C_4H_9)_3C_2H_5$$

$$Mg(C_6H_5)_2 + B(C_4H_9)_3 \rightarrow C_6H_5MgB(C_4H_9)_3C_6H_5$$

Schlesinger found that ethyllithium added equal molar quantities of trimethylborane to form a white crystalline adduct (*128*).

$$LiC_2H_5 + B(CH_3)_3 \rightarrow LiB(CH_3)_3C_2H_5$$

Hurd prepared lithium tetramethylborate by the reaction of methyllithium with trimethylborane in ethyl ether. This material was stable in very dry air, but sometimes ignited in moist air. It was soluble in ether and dissolved without reaction in water. Acidification of the aqueous solution resulted in the evolution of trimethylborane. Electrolysis of the aqueous solution gave methane, ethane, and cyclopropane (*65*).

Wittig found that triphenylborane forms stable complexes with lithium hydride and butyllithium (*70*).

Wittig first reported the preparation of a tetraphenylborate anion by the reaction of triphenylborane with phenyllithium.

$$LiC_6H_5 + B(C_6H_5)_3 \rightarrow Li^+B(C_6H_5)_4^-$$

He also prepared the hydrotriphenylborate anion by the reaction of lithium hydride with triphenylborane.

$$LiH + B(C_6H_5)_3 \rightarrow Li^+ + BH(C_6H_5)_3^-$$

A number of salts of the tetraphenylborate anion were prepared by metathesis and the usefulness of this ion in the gravimetric determination of potassium, rubidium, cesium, and ammonium ions was pointed out. The unusual compound tetraphenylphosphonium tetraphenylborate was prepared both metathetically and by the reaction of pentaphenylphosphorus and triphenylborane.

$$P(C_6H_5)_5 + B(C_6H_5)_3 \rightarrow (C_6H_5)_4P^+ + B(C_6H_5)_4^-$$

A tetraphenyl bismuthonium and a diphenyl iodonium salt were similarly prepared. He also prepared cyanotriphenylborates by the reaction of triphenylborane with metal cyanides and cyanotrihydroborates by the reaction of lithium borohydride with hydrocyanic acid. These complex cyanoborates are remarkably stable to hydrolysis and thermal decomposition.

$$B(C_6H_5) + NaCN \rightarrow Na^+ + B(CN)(C_6H_5)_3^-$$

$$LiBH_4 + HCN \rightarrow Li^+ + BH_3CN^- + H_2$$

The hydroxytriphenylborate anion and the phenylethynyltriphenyl borates were prepared similarly.

$$OH^- + (C_6H_5)_3B \rightarrow B(OH)(C_6H_5)_3^-$$

$$C_6H_5C{\equiv}C^- + (C_6H_5)_3B \rightarrow B(C{\equiv}C{-}C_6H_5)(C_6H_5)_3^-$$

These compounds were usually analyzed by decomposition with aqueous mercuric chloride (*172*).

$$(C_6H_5)_4B^- + 4HgCl_2 + 3HOH \rightarrow 4C_6H_5HgCl + 4Cl^- + 3H^+ + 3B(OH)_3$$

The use of the tetraphenylborate anion to precipitate the heavier alkali metals was patented by Heyl (*62*). A great deal of study has been made of this ion as an analytical tool for the alkali metals. The analysis may be carried out gravimetrically, titrimetrically with silver nitrate, or conductometrically (*4*, *51*, *54*, *57*).

Kraus has studied the electrolytic properties of several triarylborane complexes with small anions such as hydroxide, fluoride, and amide (*72*).

Reactions with Oxygen and Oxidizing Agents. Grummitt reported that the ease of oxidation of alkyl boranes decreased with increasing alkyl chain length and increased rapidly in the order primary, secondary, tertiary. He found indication of peroxide intermediates (*60*).

Bamford and Newitt found that trimethylborane oxidized much less readily than

tripropylborane, that the reaction was a chain process beginning and ending on walls, and that it was strongly inhibited by mixtures of trifluoroborane and water (*7*). They found indications that trimethylborane formed a 1 to 1 addition product with oxygen. Verhoek has corroborated this and isolated the adduct. He found it to be stable to air at room temperature and atmospheric pressure and to be equivalent in oxidizing power to a typical hydroperoxide of the same molecular weight (*157*).

The diarylhydroxyboranes react with chlorine water or bromine water to yield the aryldihydroxyborane according to the following equation.

$$Ar_2BOH + X_2 + H_2O \rightarrow ArB(OH)_2 + HX + ArX$$

In the presence of excess halogen the aryldihydroxyborane is decomposed to boric acid according to the equation (*1*, *103*)

$$ArB(OH)_2 + X_2 + H_2O \rightarrow ArX + HX + B(OH)_3$$

Krause reported that tribenzylborane is similar to alkylboranes in its low melting point and reactivity with oxygen. Although 1-naphthylborane is stable in air, most of the arylboranes oxidize in air to form the arylboron oxide, but do not ignite. They also react rapidly with alcohols (*78*, *79*, *80*, *82*).

$$Ar_3B + 1/2\ O_2 + H_2O \rightarrow ArBO + 2ArOH$$

Phenyldihydroxyborane reacts with hydrogen peroxide to yield phenol and boric acid. It also reacts with 50% sodium hydroxide, water under pressure, or boiling concentrated hydrochloric acid to give benzene and boric acid (*1*).

$$C_6H_5B(OH)_2 + H_2O_2 \longrightarrow C_6H_5OH + B(OH)_3$$

$$+ H_2O \xrightarrow{150^\circ\ C.} C_6H_6 + B(OH)_3$$

The diarylhydroxyboranes react with hydrogen peroxide to yield aryldihydroxyboranes according to the equation:

$$R_2BOH + H_2O_2 \rightarrow RB(OH)_2 + ROH$$

In the presence of excess hydrogen peroxide boric acid is formed (*101*):

$$RB(OH)_2 + H_2O_2 \rightarrow ROH + B(OH)_3$$

The acid dissociation constants of a large number of the aryldihydroxyboranes have been studied (*173*).

Several aryldihydroxy boranes are rapidly oxidized by alkaline potassium permanganate at room temperature. Both the 1- and 2-naphthyl derivatives give phthalic acid. *o*-Tolyl and *o*- and *p*-phenetyl derivatives are also rapidly oxidized. The rate of oxidation with *m*-phenetyl is moderate, while phenyl and *m*- and *p*-tolyl are resistant to oxidation of the benzene ring. The reaction probably proceeds through the removal of the dihydroxyboryl group by oxidation. Phenols are produced which are in general rapidly oxidized (*10*).

The tolyldihydroxyboranes are oxidized by potassium permanganate to the carboxylphenyldihydroxyborane (*71*).

Benzyl- and naphthyldihydroxyboranes reduce silver nitrate (*70*, *108*).

$$C_{10}H_7B(OH)_2 + 2Ag^+ + 2HOH \rightarrow C_{10}H_7OH + B(OH)_3 + 2Ag + 2H^+$$

Reactions with Ammonia and Amines

The reactions of alkylboranes with ammonia and amines have been studied extensively. Frankland first reported the adduct of triethylborane and ammonia (*53*).

Copley first discussed the isosterism of boron-nitrogen compounds with carbon compounds (*38*). Brown has made an extensive study in this field and has shown steric effects on many organic reaction mechanisms by using sterically similar alkyl-

borane-alkylamine reactions. As a result the stabilities and dissociation pressures of many amine-boranes have been measured (*17*).

He reports that trimethylborane and triethylborane are most easily handled and purified as the trimethylamine and ammonia adducts, respectively. The trimethylborane was freed from trimethylamine by a series of rapid distillations. The triethylborane was freed from ammonia by treatment with hydrogen chloride (*16*).

Schlesinger reports that the alkyldiboranes add two moles of ammonia and that the stability of the diammoniates of methyldiborane, dimethyldiborane, trimethyldiborane, and tetramethyldiborane to pyrolysis and disproportionation is greater than that of the methyl diboranes themselves. The stability increases with increasing number of methyl groups. On pyrolysis these materials may be converted to B-methyl aminoboranes and borazines (*138, 139*)—e.g.

$$(CH_3)_4B_2H_2 + 2NH_3 \longrightarrow 2H_3N : B(CH_3)_2H$$

$$H_3N : B(CH_3)_2H \xrightarrow{200^\circ C.} H_2NB(CH_3)_2 + H_2$$

$$H_2NB(CH_3)_2 \xrightarrow{350^\circ C.} CH_4 + 1/3\ (HNBCH_3)_3$$

Trimethylamine reacts with trimethylborane to form a 1 to 1 adduct. Trimethylamine reacts with tetramethyldiborane to form trimethylamine-dimethylborane. Trimethylamine and symmetrical dimethyldiborane give trimethylamine-methylborane. The stability of these compounds to decomposition into the original reactants decreases with the increasing number of methyl groups on boron. Stability to disproportion to trimethylamine-trimethylborane and trimethylamine-borane increases with increasing numbers of methyl groups on boron. In reaction with hydrogen chloride, increased methylation of the boron increases the rate at which hydrogen is liberated (*139*).

$$(CH_3)_3N + B(CH_3)_3 \rightleftharpoons (CH_3)_3N : B(CH_3)_3$$

$$2(CH_3)_3N + (CH_3)_4B_2H_2 \rightleftharpoons 2(CH_3)_3N : BH(CH_3)_2$$

$$2(CH_3)_3N + CH_3HBH_2BHCH_3 \rightleftharpoons 2(CH_3)_3N : BH_2CH_3$$

$$(CH_3)_3N : BH_2CH_3 \xrightarrow{HCl} (CH_3)_3N : BCl_2CH_3 + H_2$$

$$(CH_3)_3N : BH_2CH_3 \longrightarrow (CH_3)_3N : B(CH_3)_3 + (CH_3)_3N : BH_3$$

Wiberg found that condensation of equal molar amounts of trimethylborane and aniline formed a crystalline adduct. When this was heated to 300°C., two products were formed, phenylaminodimethylborane and phenyliminomethylborane. This product may trimerize to the borazine (*164*).

$$C_6H_5NH_2 + B(CH_3)_3 \rightarrow C_6H_5H_2N : B(CH_3)_3 \xrightarrow{300^\circ C.} 2CH_4 + C_6H_5N{\equiv}BCH_3$$

Burg found that trimethylboroxin reacts with ammonia to form adducts having 1 mole of ammonia and 2 moles of ammonia per mole of trimethylboroxin, respectively. Trimethylamine forms a 1 to 1 adduct with trimethylboroxin (*20*).

Miscellaneous Reactions. Tetramethyldiborane reacts with methyl hydrogen sulfide to form the new liquid compound methiodimethylborane (*26*).

$$(CH_3)_4B_2H_2 + 2HSCH_3 \rightarrow 2(CH_3)_2BSCH_3$$

Methiodimethylborane has also been prepared from methyl hydrogen sulfide and dimethylbromoborane. This material decomposes slowly to trimethylborane and less volatile materials (*29*).

$$(CH_3)_2BBr + HSCH_3 \rightarrow HBr + (CH_3)_2BSCH_3 \rightarrow (CH_3)_3B + ?$$

Trimethylphosphine forms a 1 to 1 adduct with trimethylborane (*18*)

$$(CH_3)_3P + B(CH_3)_3 \rightarrow (CH_3)_3P : B(CH_3)_3$$

A number of reactions of trialkylboranes with other compounds have been described. Burg has studied the reactions with phosphine and alkylphosphines extensively. He has found that they may be pyrolyzed to trimeric phosphinoboranes. These products are extremely stable to thermal and atmospheric decomposition (*28*).

Chatt found evidence for the lattice compound $3C_2H_4 \cdot 2(BCH_3)_3$ in the solid system ethylene-trimethylborane. He reported no association in the liquid phase (*31*).

The benzyl- and aryldihydroxyboranes are readily cleaved by mercuric chloride to form the arylmercuric chloride and boric acid (*70, 71*).

$$HOH + H_3CC_6H_4B(OH)_2 + HgCl_2 \rightarrow CH_3C_6H_4HgCl + B(OH)_3 + HCl$$

Phenyldihydroxyborane is cleaved by hot mercurous bromide solutions to give phenylmercury bromide. Cupric chloride gives phenyl chloride, cupric bromide gives phenyl bromide, and cupric cyanide give some phenyl cyanide, most of the product being benzene in the latter case. Cadmium bromide and zinc chloride give benzene and phenyldihydroxyborane. Phenyldihydroxyborane can be nitrated in sulfuric acid below −70°C. to give *m*-nitrophenyldihydroxyborane. This material is cleaved by cupric chloride, mercuric chloride, bromine, and hydrogen peroxide in a manner similar to phenyldihydroxyborane. Hot aqueous solutions of beryllium, magnesium, or calcium chlorides do not attack phenyldihydroxyborane (*1*). The aryldihydroxyboranes react with thallic chloride and thallic bromide to give the diarylthallium halide (*104*).

$$2HOH + 2ArB(OH)_2 + TlCl_3 \rightarrow Ar_2TlCl + 2B(OH)_3 + 2HCl$$

Triphenylborane is stable in nitrogen or carbon dioxide (*78*).

Uses of Alkyl- and Arylboranes

Trimethylborane is more stable and more sensitive than trifluoroborane in proportional neutron counters (*61*).

A condensation product of chlorovinyldichloroborane with poly(vinyl alcohol) has been patented as a polymer which does not swell in water (*127*).

Martin has patented the preparation of thin boron coatings by the pyrolysis of alkylboranes over an object (*100*).

Bowman has calculated the theoretical exhaust velocity of triethylborane as a rocket fuel (*13*).

Grisdale has found the pyrolysis of tripropylborane useful in the preparation of boron-carbon coatings. A film of boron and carbon is deposited on a ceramic support at approximately 1000°C. (*58*).

Lincoln has patented the addition of alkylalkoxyboranes to hydrocarbon oils (*94*).

Darling has found that trialkylboranes reduce the octane requirement increase due to leaded gasolines to 0 to 40% of the normal value (*63*).

Smith has patented the use of alkylboranes to stabilize amines against discoloration (*145*).

Safford has patented an elastic polysiloxane containing small amounts of boron hydrides. Diphenyldecaborane is suggested as the boron source (*126*).

Rosen has suggested the use of ethylamine-triphenylborane as an oxidation inhibitor in lubricants and gasoline (*121*).

Stout and Chamberlain extensively investigated alkylboron oxygen polymers analogous to silicones and found them to be both heat- and moisture-sensitive (*150*).

Safford and Hurd have patented a polymer using a boron hydride as a polymerization catalyst. Diphenyldecaborane is suggested as one of the catalysts (*126*).

Nijimoto has patented the preparation of a heat-resistant film from phenyldifluoroborane and diphenyldichlorosilane (*111*).

Carbon Monoxide Derivatives

The formation of carbon monoxide–borane was first observed by Burg when diborane was treated with high concentrations of carbon monoxide under pressures.

$$B_2H_6 + 2CO \rightleftharpoons 2BH_3CO$$

The product was isolated at liquid nitrogen temperatures. It decomposed easily at room temperatures. The rates of decomposition were studied (*21, 27*).

Burg has reported that pentaborane(11) reacts with carbon monoxide to form apparently carbon monoxide–triborane. This material decomposes to carbon monoxide and a colorless oil which reacts with carbon monoxide–borane to give a 60% yield of tetraborane. Unlike carbon monoxide–borane, it absorbs trimethylamine without loss of carbon monoxide (*26*).

$$B_5H_{11} + CO \rightarrow B_3H_7CO + ?$$

$$B_3H_7CO + BH_3CO \rightarrow B_4H_{10} + 2CO$$

$$B_3H_7CO + N(CH_3)_3 \rightarrow ?$$

Later work has indicated that the previously reported carbon monoxide–polyborane may be B_4H_8CO. It has been made in improved yield from tetraborane instead of pentaborane (*11, 29*).

$$B_4H_{10} + CO \rightarrow B_4H_8CO?$$

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Preparation, Properties, and Uses of Benzeneboronic Acid

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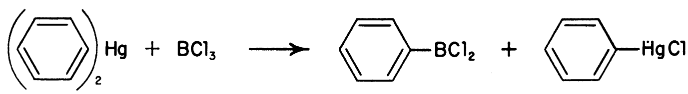
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The purpose of this study was the development of a commercially practical process for the preparation of benzeneboronic acid based on known laboratory methods. The reaction of boron trifluoride with phenylmagnesium bromide was investigated briefly. The process finally developed, involving the reaction of phenylmagnesium bromide and methyl borate to give yields of up to 100% of benzeneboronic acid, was shown to be of general applicability by the preparation of *p*-chlorobenzene- and 1-naphthalene-boronic acids in high yields. This paper presents: the effect of process variables on the yield of benzeneboronic acid; a unifying discussion of the important chemical and physical aspects of the process; new physical and chemical data concerned with the preparation and properties of benzeneboronic acid; and a discussion of the reactions of benzeneboronic acid and its immediate derivatives.

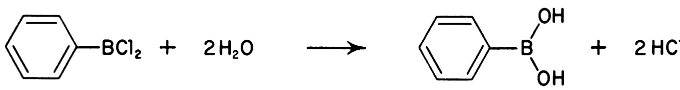
The nomenclature for boron compounds is in a state of flux at the present time. The following list of boron compounds discussed in this paper indicates the nomenclature used. The reader is referred to the following references for boron nomenclature (*8, 64, 65, 68, 69, 72*).

$C_6H_5B(OH)_2$	Benzeneboronic acid
$C_6H_5B(OCH_3)_2$	Dimethyl benzeneboronate
$C_6H_5BCl_2$	Benzeneboronyl dichloride
$(C_6H_5)_2BOH$	Dibenzeneborinic acid
$(C_6H_5)_2BOCH_3$	Methyl dibenzeneborinate
$(C_6H_5)_3B$	Triphenylborane
$(C_6H_5)_4B^-Li^+$	Lithium tetraphenylborohydride

Background. Benzeneboronic acid was first reported by Michaelis and Becker (*58, 59*), who prepared benzeneboronyl dichloride by heating boron trichloride and diphenyl mercury at 180° to 200°C. in a sealed tube (Equation 1). Benzeneboronyl dichloride was found to hydrolyze easily, giving benzeneboronic acid (Equation 2).



(1)



(2)

Michaelis and Becker reported the melting point of benzeneboronic acid to be 204°C., but later, Michaelis and Behrens (*60*) changed this to 216°C.

Diphenylmercury has been shown to react smoothly with boron tribromide under reflux to give benzeneboronyl dibromide and dibenzeneborinyl bromide (*31, 61*).

Khotinsky and Melamed (*35*) were the first to describe the preparation of boronic acids from Grignard reagents and borate esters. They reported that ethyl, *n*-propyl, isobutyl, and isoamyl borates gave about 50% yields of boronic acids or their esters, when the alkyl ester was added to the Grignard reagent at 0°C. They also claimed the formation of some by-product toluene when methyl borate was used, but this could not be confirmed by Gilman and Vernon (*27*).

Krause and Nitsche (*39, 40*) investigated the reaction of boron trifluoride and Grignard reagents. They found that an excess of phenylmagnesium bromide gave triphenylborane, but an excess of boron trifluoride gave a mixture of triphenylborane, dibenzeneborinyl fluoride, and benzeneboronyl difluoride. The difluoride yielded the boronic acid when hydrolyzed.

Gilman and Vernon (*27*) investigated the preparation of benzeneboronic acid using the procedures of Khotinsky and Melamed (*35*). Triphenyl borate and phenylmagnesium bromide gave 40% of phenol, 16.4% of benzeneboronic acid, and 1.3% of biphenyl. They reported an 86% yield of the boronic acid from the reaction of a 0.25-mole run of methyl borate and phenylmagnesium bromide, but with more concentrated solutions the yield was reduced to 58% and a 30% yield of benzene was obtained. The benzene was supposedly obtained by hydrolysis of unreacted Grignard reagent.

König and Scharrnbeck (*38*) reported the preparation of benzeneboronic acid and dibenzeneborinic acid by adding isobutyl borate to the Grignard reagent at 0°C.

Seaman and Johnson (*71*) could not repeat the work of Gilman and Vernon. They stated that the methyl borate must be free of methanol "since the latter caused a marked diminution of the yield, apparently greater than could be accounted for on the basis of the Grignard destroyed." Furthermore, these authors reported that an inverse Grignard reaction gave better yields. Subsequently, Bean and Johnson (*3*) were able to increase the yield of benzeneboronic acid considerably by using the more easily purified butyl borate and effecting the reaction at −60°C. In several runs yields ranged from 50 to 60%. More concentrated solutions gave lower yields (42 to 47%).

Branch and his coworkers (*5, 6, 8, 23, 88, 89*), Kuivila and his coworkers (*41–49*), and others (*9, 74, 76, 79*) have used the procedure of Bean and Johnson for the preparation of benzeneboronic acid and other areneboronic acids. The yields were generally about 50%.

During a study of the preparation and physical properties of benzeneboronic acid, Hutto (*31*) obtained yields of about 40% by adding phenylmagnesium bromide to methyl borate cooled with an ice bath. Hutto also checked the procedures of Khotinsky and Melamed (*35*) and obtained 10.5% yield; the procedure of Krause and Nitsche (*39, 40*) gave about 10% yield.

Mel'nikov (*55*) used the procedure of König and Scharrnbeck (*38*), but Letsinger and Skoog (*52*) preferred an inverse procedure and low temperatures.

Another synthetic approach, which apparently gives lower yields, involves the reaction of phenyllithium with a borate ester. Brindley, Gerrard, and Lappert (*9*)

reported a 36% yield of benzeneboronic acid using butyl borate at −80°C. Letsinger and Skoog (*52*) reported a 41% yield of butyl dibenzeneborinate and a 13% yield of ethylene glycol benzeneboronate from the reaction of 2 moles of phenyllithium with butyl ethylene glycol borate.

Terminology. The following terms are used in the Discussion and Experimental sections of this paper:

Fast reaction	=	Reactants added as rapidly as possible while keeping the reaction temperature constant (0.33 hour or less to add 3.00 moles)
Slow reaction	=	Reactants added slowly (0.75 to 4.0 hours to add 3.00 moles)
3-Mole reaction	=	Three moles of Grignard (as 3.0*M* solution) + 3 moles of methyl borate in 1500 ml. of ether

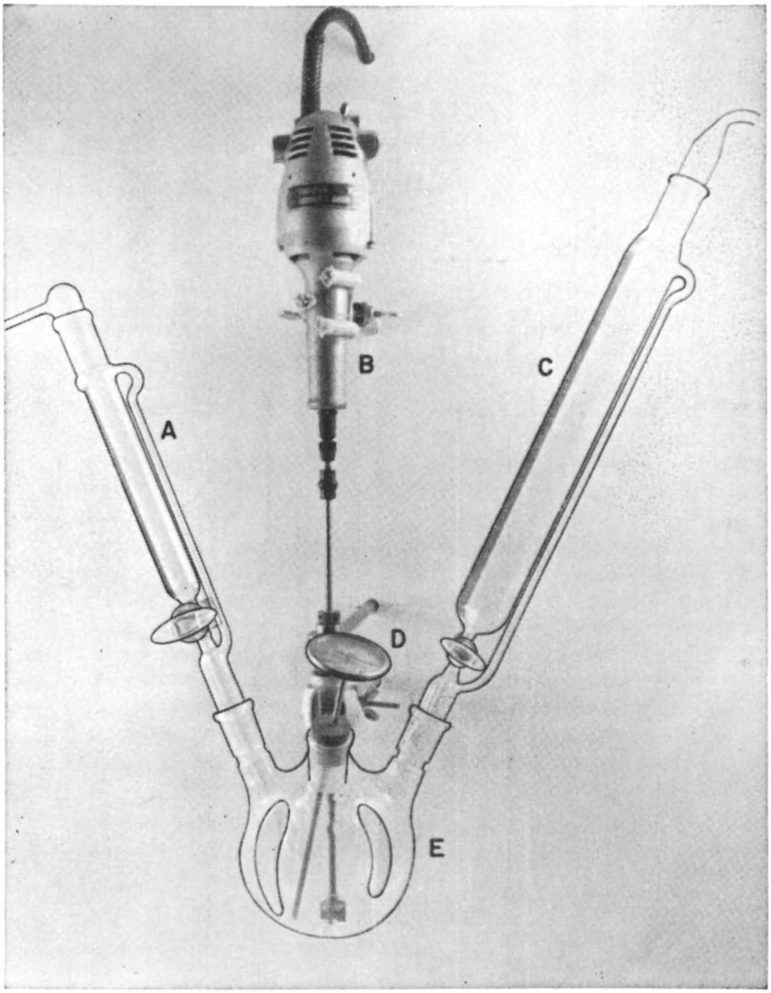


Figure 1. Equipment for study of methyl borate and phenylmagnesium bromide reaction

A. Methyl borate addition buret
B. Stirring motor
C. Grignard addition buret
D. Thermometer
E. Morton flask

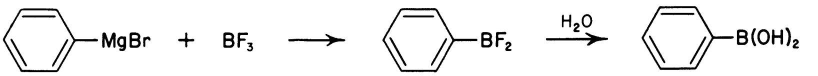
2-Mole reaction = Two moles of each reactant but the same total volume (diluted with ether) as a 3-mole reaction
1-Mole reaction = One mole of each reactant but the same total volume as a 3-mole reaction

Experimental

Reagents. The ether used was Mallinckrodt A. R. grade, stored over sodium. Phenylmagnesium bromide was obtained from Arapahoe as a 3.0*M* solution in diethyl ether. Different batches, analyzed by the method of Gilman (*26*), varied between 3.0 and 3.2*M*. The material was used as received (based on the analysis) or diluted with ether as necessary. Boron trifluoride was obtained from Matheson. Boron trifluoride–etherate was prepared by passing the gas into cooled ether until the weight indicated the correct amount of boron trifluoride had been absorbed. Methyl borate was commercial anhydrous material from American Potash & Chemical Corp. It was found by analysis to contain 99.0% of ester. The methyl borate was purified before use by fractionation in a 30-plate column. *p*-Chlorophenylmagnesium bromide was prepared from *p*-bromochlorobenzene; 1-naphthylmagnesium bromide was prepared from 1-bromonaphthalene in ether-benzene solvent (*26*).

Equipment. The equipment used is shown in Figure 1. For small runs (1-liter flask) the stirrer used was a Labline Stir-O-Vac (from Labline, Inc., 217 North Des Plaines St., Chicago 6, Ill.) stirring at about 5000 r.p.m. For larger runs (5-liter flask), a Premier, 1-inch diameter, Duplex Dispersator (obtained from Premier Mill Corp., Geneva, N. Y.) stirring at about 7500 r.p.m. was used.

Reaction of Boron Trifluoride Etherate and Phenylmagnesium Bromide. The reaction of boron trifluoride and phenylmagnesium bromide (Equation 3) was briefly investigated using the procedure of Krause and Nitsche (*40*). In each experiment the solids fumed on first exposure to air indicating the presence of triphenylborane; the



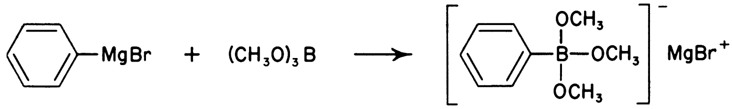
(3)

boron content of the product, isolated in 0 to 46% yield, generally corresponded most closely to dibenzeneborinic acid or its anhydride. These results are in accord with the observations of Hutto (*31*).

This line of investigation was dropped in favor of the more easily handled reaction with methyl borate.

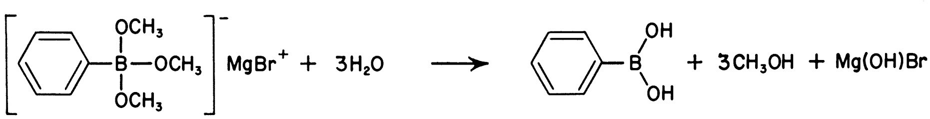
Reaction of Phenylmagnesium Bromide and Methyl Borate. The preparation of benzeneboronic acid from phenylmagnesium bromide and methyl borate can be represented by Equations 4, 5, and 6.

Reaction.



(4)

Hydrolysis.



(5)

Neutralization.

$$Mg(OH)Br + \tfrac{1}{2}H_2SO_4 \rightarrow \tfrac{1}{2}MgBr_2 + \tfrac{1}{2}MgSO_4 + H_2O \qquad (6)$$

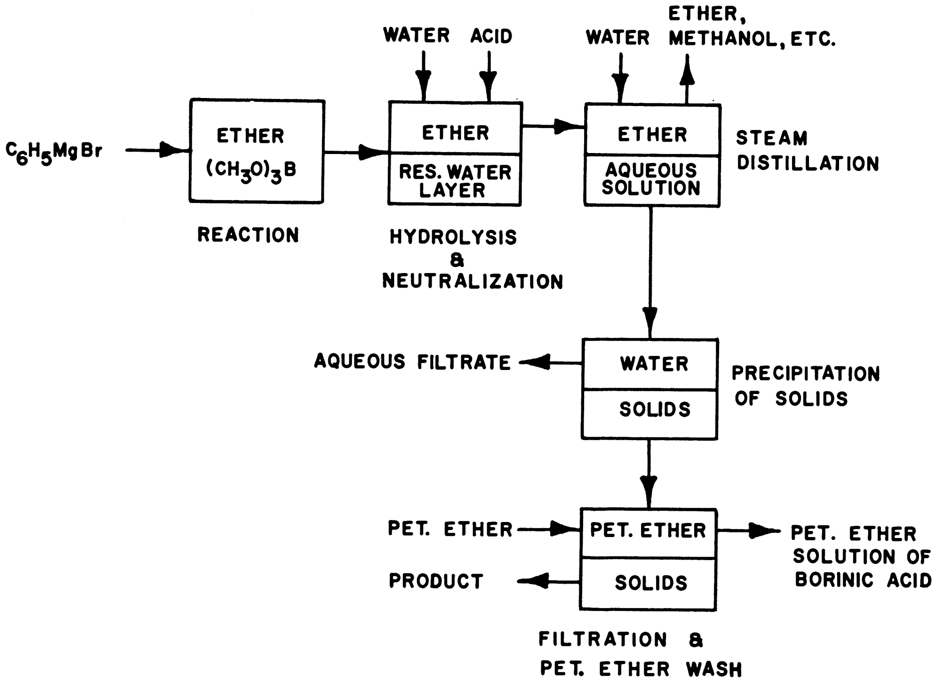


Figure 2. Process flow diagram for preparation of benzeneboronic acid

Figure 2 shows a simplified process flow diagram of the process investigated.

The process variables investigated were reaction temperature, rate of addition of Grignard to methyl borate, mode of addition and concentration of reactants, effect of impurities in the methyl borate, and the procedure for isolating benzeneboronic acid.

The procedure for isolating benzeneboronic acid used throughout this investigation involved extraction of the product from the hydrolyzed and neutralized reaction mixture with ether, steam distillation of ether and volatile impurities, crystallization of the product, and petroleum ether wash of the isolated solids to remove dibenzeneborinic acid. This is a considerably simpler process than any previously reported.

Depending on the experimental conditions, various products were formed during the investigation of the process shown in Figure 2. For example, in experiments at 0°C., about 20% of the methyl borate could be accounted for in the aqueous residue and varying amounts of the Grignard could be accounted for as benzene. Qualitatively, about 2 to 3% phenol and up to about 5% biphenyl were observed as products of experiments conducted at higher temperatures (15° to 25°C.). The benzene, phenol, and biphenyl were removed during the steam distillation step. In all experiments where the Grignard was added to the methyl borate, the varying amounts of dibenzeneborinic acid formed were separated from the benzeneboronic acid by washing the filtered solids with petroleum ether.

Addition of Phenylmagnesium Bromide to Methyl Borate. Effect of Rate of Addition of Phenylmagnesium Bromide. During the early part of this work, the Grignard reagent was added to the methyl borate relatively slowly in accordance with established literature procedures (*71*) The average yield (Table I-1) for three slow runs at 0°C. was 46.8%.

A group of nine 3-mole runs was made at 0°C. in which the Grignard was added as rapidly as possible while maintaining a constant temperature (Table I-2); the

Table I. Addition of Phenylmagnesium Bromide to Methyl Borate 0°C.
(3.0-mole reaction)

Run No.	Addn. Time, Hr.	Solids		Aq. Filtrate		% Yield	
		Grams	% B	Grams	% B	Boronic acid	Borinic acid
1[a,b]	1.23	154	8.68	885	0.48	46.8	—
2[a,c]	0.18	179	8.35	1086	0.35	53.3	18.2[d]
3[e,f]	0.15	194	9.01	942	0.34	60.2	16.8[g]
4[h]	0.20	167	8.69	1011	0.30	51.5	27.7
5[i]	0.20	165	8.65	959	0.28	50.5	31.7

[a] Methyl borate purified and stored before use.
[b] Slow reaction, average of 3 runs.
[c] Fast reaction, average of 9 runs.
[d] Average of 5 runs.
[e] Methyl borate distilled directly into apparatus.
[f] Fast reaction, average of 5 runs.
[g] Average of 4 runs.
[h] Fast reaction, 0.953 gram of methanol added to freshly distilled methyl borate.
[i] Fast reaction, 0.613 gram of boric acid added to freshly distilled methyl borate.

Table II. Fast Addition of Phenylmagnesium Bromide to Methyl Borate
3.0-mole reaction (distilled methyl borate)

Run No.	Reaction Temp., °C.	Addn. Time, Hr.	Solids		Aq. Filtrate		% Yield	
			Grams	% B[a]	Grams	% B	Boronic acid	Borinic acid
1	0	0.20	180	9.49	1190	0.33	60.7	—
2	0	0.12	194	9.01	1386	0.27	63.3	—
3	0	0.15	196	8.40	908	0.31	56.9	14.7
4	0	0.18	215	8.35	270	0.51	57.2	14.0
5	0	0.12	187	9.78	957	0.28	62.9	19.3
6	−15	0.15	249	8.53	586	0.37	69.5	—
7	−30	0.20	275	8.66	327	0.34	75.6	—
8	−60	2.50	367	6.76	1295	0.21	85.3	—
9	−62	1.03	292	8.55	477	0.36	80.2	1.8

[a] Theoretical % boron, 8.87.

average yield was 53.3%. Thus, there was a definite increase in yield when the reaction was allowed to proceed rapidly.

Effect of Concentration. The average yield for 1.0-mole runs made at 0°C. using fast addition of Grignard was 64.5%, and a yield of 60% was obtained in one 2.0-mole run. The average yields at 0°C. for the 3.0-, 2.0-, and 1.0-mole runs are plotted *vs.* mole–per cent of methyl borate in ether at the start of the reaction in Figure 3. This

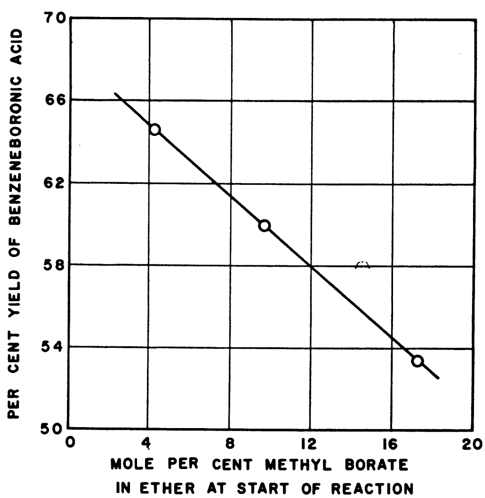


Figure 3. Variation in yield of benzeneboronic acid with concentration
Fast addition, 0°C., undistilled methyl borate

quantitatively shows the advantage of dilute solutions for the addition of Grignard to methyl borate.

Effect of Impure Methyl Borate. Although all the methyl borate was carefully purified by fractionation, it was stored in bottles until used. The authors discovered, however (Table II-5), when the methyl borate was distilled directly into the apparatus, that the yield at 0°C. was increased from 53.3 to 62.9%.

The effect of either methanol or boric acid as impurities in the methyl borate was checked by adding small quantities of these materials to individual runs made at 0°C. and using fast addition of phenylmagnesium bromide to methyl borate. The data are summarized in Table I-4, 5. The yield was reduced from 62.9 to 51.5% with the addition of 0.953 gram of methanol, and to 50.5% with the addition of 0.613 gram of boric acid. The decrease in yield is considerably in excess of the Grignard reagent that would be destroyed by these impurities (*71*).

Effect of Temperature. The effect of reaction temperature was first investigated using slow addition of Grignard reagent to methyl borate which was purified but stored before use. The data are given in Table III. Figure 4 (curve *A*) shows a least squares

Table III. Slow Addition of Phenylmagnesium Bromide to Methyl Borate

3.0-mole reaction (undistilled methyl borate)

Reaction Temp., °C.	Addn. Time, Hr.	Solids		Aq. Filtrate		% Yield Boronic Acid
		Grams	% B[a]	Grams	% B	
+20	1.9	140	8.48	1116	0.37	44.2
+8	3.5	134	8.78	899	0.48	42.4
+6	3.5	138	7.07	1448	0.20	40.0
+6	3.5	57.8	7.91[b]	2087	0.20	39.6
		41.0	9.03			
0	2.25	128	8.50	1088	0.33	40.9
0	0.66	195	7.88	744	0.63	52.4
0	0.78	140	9.65	822	0.49	47.2
−15	0.75	190	8.45	1233	0.18	57.9
−30	1.5	210.8	8.35	1160	0.24	62.1
−30	1.3	228	8.25	1139	0.20	65.7
−60	2.5	367	6.76	1295	0.21	85.3

[a] Theoretical % boron, 8.87.
[b] Two crops, dried and analyzed independently.

plot of the per cent yield *vs.* reaction temperature for the slow runs.

The study of the effect of reaction temperature was repeated using fast addition of Grignard reagent; the methyl borate was distilled directly into the addition buret. The data are given in Table IV and shown as the least squares line in Figure 4 (curve

Table IV. Fast Addition of Phenylmagnesium Bromide to Methyl Borate

1.0-mole runs (undistilled methyl borate)

Reaction Temp., °C.	Addn. Time, Hr.	Solids		Aq. Filtrate		% Yield	
		Grams	% B[a]	Grams	% B	Boronic acid	Borinic acid
+20	0.6	29.0	8.52	744	0.58	49.2	—
+20	0.5	53.7	8.59	475	0.36	52.3	—
+10	0.7	60.0	8.73	545	0.35	59.6	—
0	0.05	62.0	8.79	1035	0.18	67.6	16.4
0	0.83	63.5	8.56	661	0.22	63.5	—
0	0.6	62.0	8.11	810	0.22	63.0	—
0	0.5	62.5	8.42	749	0.29	63.9	—
−15	0.6	71.0	8.72	336	0.27	64.1	—
−15	0.7	69.0	8.55	566	0.24	66.0	—
−30	0.6	74.2	8.88	521	0.22	71.5	—
−30	0.7	62.7	8.79	1007	0.22	73.3	—
−65	1.75	88.0	8.82	819	0.26	88.6	—

[a] Theoretical % boron, 8.87.

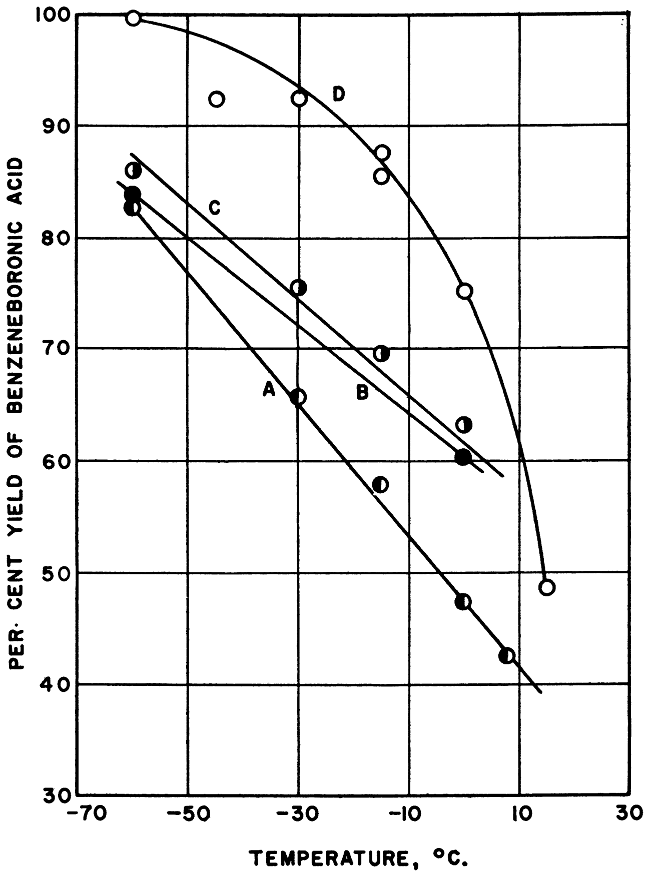


Figure 4. Variation in yield of benzeneboronic acid with reaction temperature

A. 3-mole runs, slow addition, undistilled methyl borate
B. 3-mole runs, fast addition, distilled methyl borate
C. 1-mole runs, fast addition, undistilled methyl borate
D. Fast, incremental addition

B). Using fast addition and pure methyl borate gives decided improvement in yield of benzeneboronic acid at 0°C., but very little difference in yield at —60°C.

The effect of temperature for more dilute solutions was obtained in a series of 1.0-mole runs using fast addition and purified but stored methyl borate. The data are given in Table IV and shown as a least squares line in Figure 4, curve *C*.

The data in Tables II, III, and IV, and curves *A*, *B*, and *C* in Figure 4 indicate that yields up to 88.6% of benzeneboronic acid can be obtained at —65°C.

Addition of Methyl Borate to Phenylmagnesium Bromide. One 3.0-mole run was made at 0°C. in which purified but stored methyl borate was added rapidly to phenylmagnesium bromide. The yield of benzeneboronic acid was 42.8% and of dibenzeneborinic acid, 39.9%.

Incremental Addition of Phenylmagnesium Bromide and Methyl Borate. Fast Addition. This new incremental procedure finally developed for the preparation of benzeneboronic acid is given in detail below for a 3-mole run at 0°C.

Methyl borate (336 ml., 3.0 moles) was distilled directly into one buret. Anhydrous ether (1500 ml.) was placed in the reaction flask, using dry nitrogen for pressure transfer, and then cooled to 0°C. An ethereal solution of phenylmagnesium bromide (1000 ml., 3.0 moles) was pressure-transferred (dry nitrogen) to the second buret. The reactants were added incrementally to the rapidly agitated ether, adding first methyl borate (10 ml.) then phenylmagnesium bromide (30 ml.) so as to maintain a stoichiometric ratio with only a very slight excess of methyl borate. A temperature of 0°C. was maintained with a dry ice–acetone bath during the addition. All of the reactants were added within a 15-minute period and the mixture was stirred for an additional 20 minutes before hydrolysis.

The mixture was hydrolyzed by adding distilled water (200 ml.) during 5 minutes while a temperature of 0°C. was maintained. The mixture was then neutralized with sulfuric acid (84 ml. in 1700 ml. of water) during a 15-minute period at 0°C. When the stirring was stopped, the mixture separated into two clear layers. The ether layer was removed and the aqueous layer was extracted with three 250-ml. portions of ether. The combined extracts and ether layer were transferred to a 5-liter flask, equipped with a Hershberg stirrer, modified Claisen head, and dropping funnel. Part of the ether was removed by distillation, and then distilled water (1500 ml.) was slowly added as the distillation proceeded. Distillation was continued until the head temperature reached 100°C. During this time a small quantity of biphenyl collected in the condenser. While stirring was continued the aqueous distilland was cooled rapidly with an ice bath. Benzeneboronic acid crystallized at 43°C. with a temperature rise to 45°C. Stirring was continued until the mixture had cooled to 11°C. and then the solids were removed by filtration and air dried. The resulting product (277 grams including 32 grams from filtrate, 75.8%) was a fine, white crystalline powder analyzing 8.80% of boron (8.87% theory). Only a trace of dibenzeneborinic acid was obtained.

Slow Addition. Using the procedure and ratio of reactants to solvent as described above for the fast reaction, methyl borate (28.0 ml., 0.25 mole) and phenylmagnesium bromide (78 ml., 0.25 mole) were added incrementally to a precooled ether heel (125 ml.). The reactants were added in 26 increments using the ratio of 1.0 ml. of ester per 3.0 ml. of Grignard. Initially, 1 ml. of excess methyl borate was added and after the thirteenth increment a second 1.0-ml. excess of methyl borate was added.

The reaction mixture was stirred 10 minutes after each increment and for 50 minutes after the last increment (total time, 5 hours), during which time the reaction temperature was maintained at 0°C. There was a tendency for the temperature to rise after the addition of each increment. After hydrolysis, neutralization, and extraction (see above) the ether extracts were steam distilled with 125 ml. of water. When distillation and stirring were stopped, a sizable oil layer settled to the bottom of the hot solution. When it was cooled and stirred, the benzeneboronic acid precipitated. The solids were removed by filtration, washed on the filter with two 50-ml. portions of petroleum ether, and air dried. Yield was 19.4 grams (including product in the aqueous filtrate) or 63.5%. The petroleum ether filtrate was evaporated to dryness in vacuo, yielding 6.4 grams of dibenzeneborinic acid (28.2%).

Effect of Reaction Temperature Using Fast Incremental Addition. In order to evaluate the effect of temperature on the yield of benzeneboronic acid when incremental addition is being used, a series of 0.5-mole runs was made at various temperatures (−60°, −45°, −30°, −15°, +15°C.). The value used for 0°C. was that obtained from the 3-mole run previously described. In each case, the addition time was as rapid as possible, but the variation in the temperature difference between the dry ice–acetone bath and the desired reaction temperature precluded equal rates of addition. The apparatus and procedure were the same as those described above.

Only negligible quantities of dibenzeneborinic acid were obtained at temperatures of −15°C. or less, but considerable borinic acid was obtained at +15°C. The data

given in Table V and Figure 4 indicate that essentially quantitative yields are obtained at −60°C., with the formation of only trace amounts of borinic acid.

Table V. Effect of Reaction Temperature on Yield of Benzeneboronic Acid

(Incremental fast addition of phenylmagnesium bromide and methyl borate)

Run No.	Reaction Temp., °C.	Addn. Time, Hr.	Solids		Filtrate		Total Benzeneboronic Acid		Borinic Anhydride, Grams
			Grams	% B[a]	Grams	% B	Grams	% Yield	
1	+15	0.20	24.9	8.08	238	0.260	29.7	48.7	11.2
2[b]	0	0.25	246.6	8.80	1117	0.260	277.4	75.8	—
3	−15	0.25	52.3	8.28	218	0.181	53.3	87.5	1.68
4	−15	0.25	46.1	8.42	236	0.190	52.2	85.6	1.35
5	−30	0.25	56.2	8.16	257	0.160	56.3	92.3	0.647
6	−45	0.38	52.1	8.77	226	0.184	56.2	92.2	0.417
7	−60	0.90	55.8	8.73	287	0.180	60.7	99.5	0.327

[a] Theoretical % boron, 8.87.
[b] Three-mole incremental described in text.

Reaction of Other Grignard Reagents with Methyl Borate. *p*-Chlorobenzene- and 1-naphthaleneboronic acids were prepared in 81 and 68% yields, respectively, from the appropriate Grignard reagents and methyl borate at 0°C. using the incremental procedure described. The data and results are given in Table VI.

Table VI. Reaction of *p*-Chlorophenyl- and 1-Naphthylmagnesium Bromide with Methyl Borate

(Incremental procedure)

Boronic Acid	Grignard Reagent			$(CH_3O)_3B$, Mole	Addn. Time, Min.	Ether Heel, Ml.	Reaction Temp., °C.	Yield, %
	Concn., *N*	Ml.	Mole					
p-Chlorobenzene-	1.45	172.5	0.25	0.25	25	100	0	81
1-Naphthalene-[a]	0.685	365	0.25	0.25	16	100	0	68

[a] Because 1-naphthaleneboronic acid is decomposed by boiling water (*60*), the ether extracts were distilled with benzene to give the anhydride as the product isolated.

Purification of Benzeneboronic Acid and Anhydride. Benzeneboronic acid is readily converted to the anhydride and, therefore, care must be exercised to obtain the boronic acid free of the anhydride. The best procedure for obtaining a spectroscopically pure sample is to recrystallize the acid from water using a little charcoal. The acid is then dried with a slow stream of air almost saturated with water. If the acid is finely ground and spread thinly it will undergo almost complete dehydration on standing overnight in the laboratory (relative humidity 30 to 40%).

Benzene should not be used as a solvent for the crystallization of benzeneboronic acid. French and Fine (*25*) observed a molecular weight in benzene higher than monomer. The authors' solubility data (see below) and the fact that benzeneboronic acid can be converted easily to the anhydride by azeotropic distillation of water with benzene suggest that conversion to the anhydride occurs to some extent on crystallization of the acid from benzene. Unfortunately, melting point cannot be used as a criterion of purity, as the observed melting point 215° to 216°C. is actually that of the anhydride.

Pure anhydride can be simply prepared from purified boronic acid by azeotropic dehydration with toluene. The anhydride precipitates slowly from the cooled solution as a white microcrystalline powder.

Physical Properties. The work of French and Fine (*25*) and Kinney and Pontz (*36, 37*) indicates that benzeneboronic acid is monomeric and that the anhydride is trimeric.

The reported physical data for benzeneboronic acid are collected in Table VII.

Table VII. Physical Properties of Benzeneboronic Acid

Property	Value	Reference
Melting point, °C.	215–216[a]	—
$K_a \times 10^{10}$	13.7 (H_2O) 1.97 (25% C_2H_5OH)	(*8*)
Polarization, P_∞	91.94 (Benzene) 98.28 (Dioxane)	(*63*)
Dipole moment, $\times 10^{18}$	1.64 (Benzene) 1.72 (Dioxane)	(*63*)

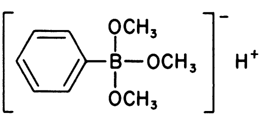
[a] M.p. of anhydride.

The polarization and dipole moment (*63*) for benzene solutions of the acid are probably a little low due to the tendency of the acid to dehydrate.

Infrared Spectra. The infrared spectrum of benzeneboronic acid is shown in Figure 5 and that for the anhydride in Figure 6. The three bands at 1023, 1086, and 1175 cm.$^{-1}$ are characteristic of the anhydride. The bands at 1333 cm.$^{-1}$ in the spectra of the acid and anhydride are probably B—O stretching (calculated, 1350 cm.$^{-1}$). The shoulder in the anhydride spectrum at 1252 cm.$^{-1}$ and in the boronic acid spectrum at 1250 to 1270 cm.$^{-1}$ has been tentatively assigned to B—C stretching (calculated, 1247 cm.$^{-1}$). Benzeneboronyl dichloride and dimethyl benzeneboronate also show absorption in this region.

Solubility of Benzeneboronic Acid and Anhydride. The solubility of benzeneboronic acid as a function of temperature (0° to 45°C.) was determined in benzene, carbon tetrachloride, ether (35°C.), methanol, water, petroleum ether, and xylene (Figure 7), and the solubility of the anhydride was determined in benzene, toluene, and xylene (Figure 8).

The solubility of the acid in methanol and water is apparently a straight line within the temperature range studied. The very high solubility in methanol suggests the possibility of complex formation I [cf. Syrkin and Dyatkina (*78*)].



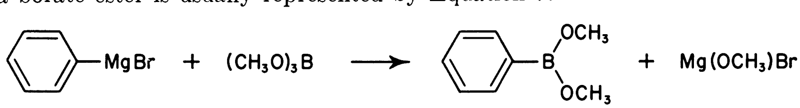
I

A comparison of the solubility of the acid and anhydride in benzene and xylene shows the anhydride to be more soluble, but in each case the slope of the curve for the acid increases with temperature, indicating possible dehydration.

The solubility curves fit the data with a maximum deviation of 15% except for carbon tetrachloride, petroleum ether, and xylene in which the solubilities are very low at low temperatures. In these cases, the possibility for error increases because of the difficulty of accurately determining the small quantities of boron in the analytical samples.

Discussion

Occurrence of Tetracoordinate Complex. The reaction of a Grignard reagent with a borate ester is usually represented by Equation 7.



(7)

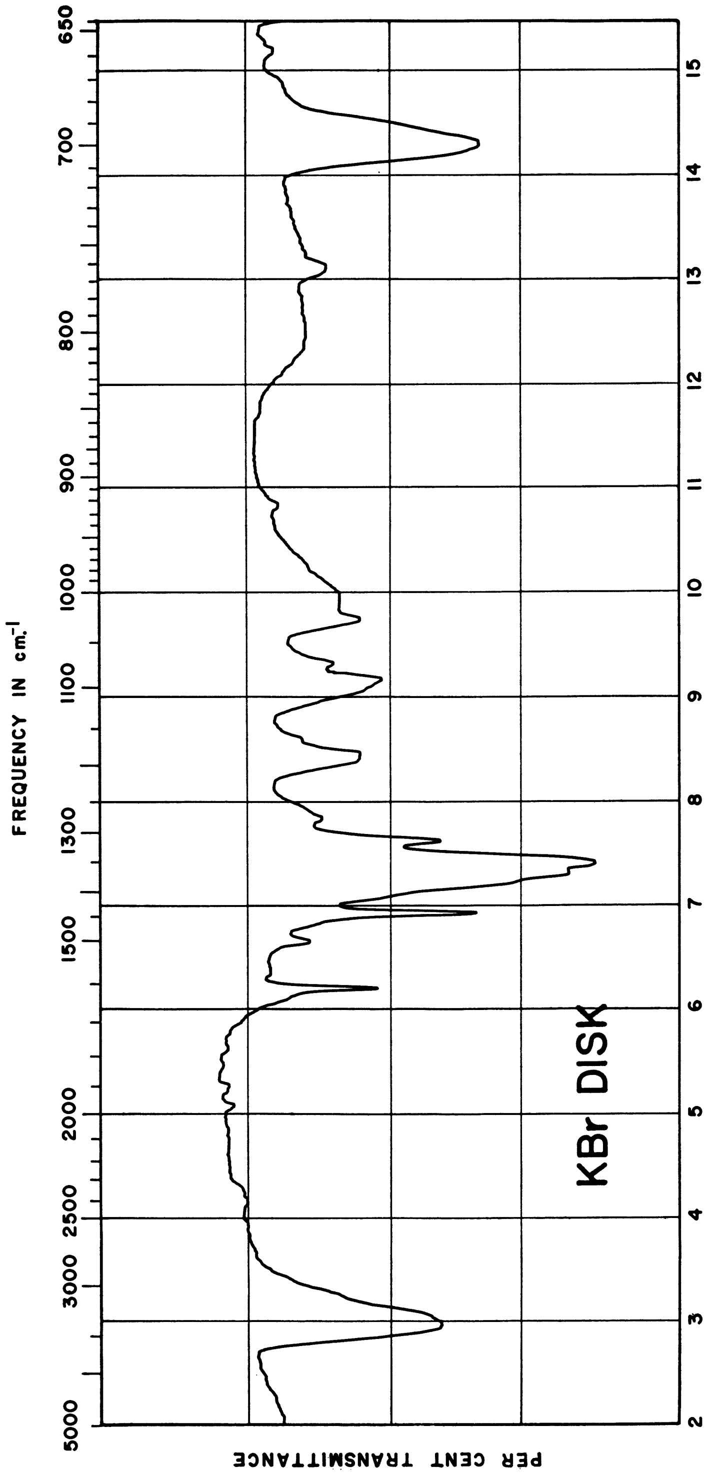


Figure 5. Infrared spectrum of benzeneboronic acid

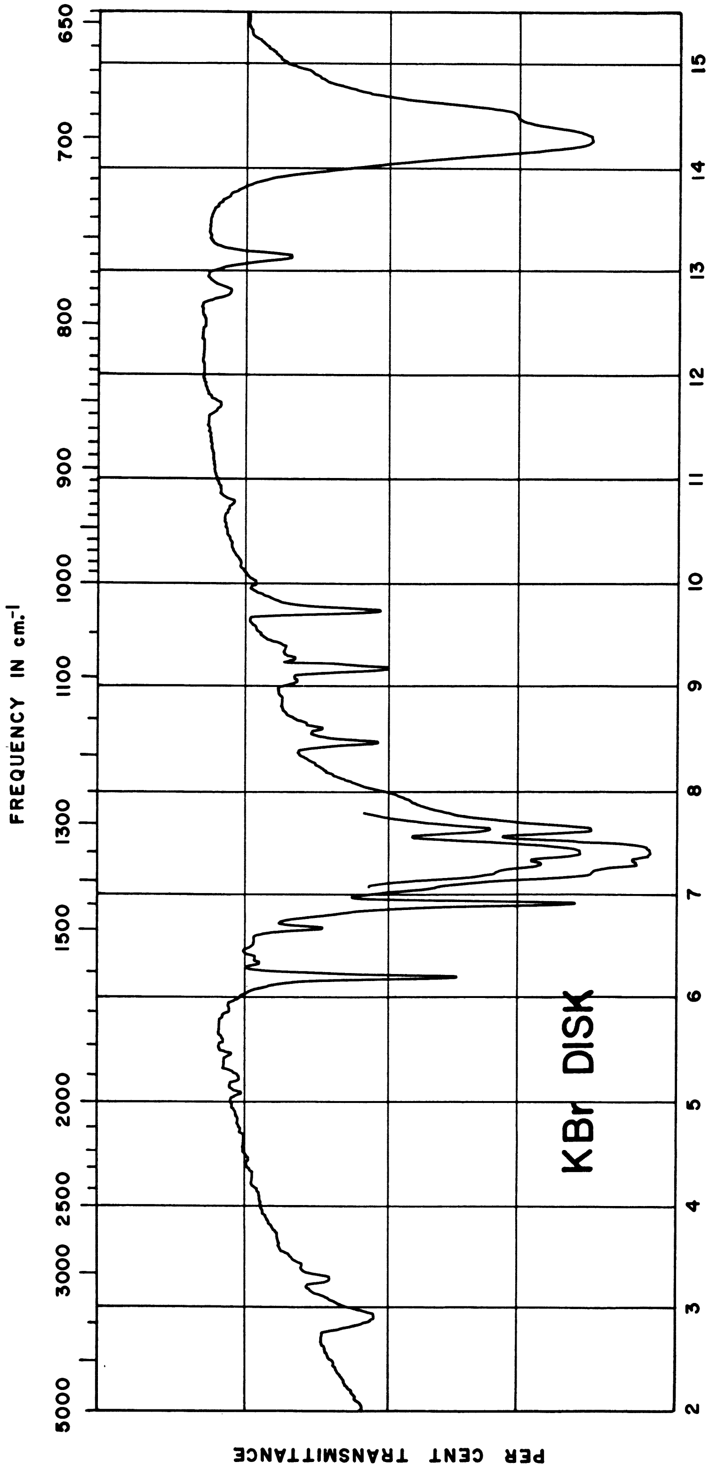


Figure 6. Infrared spectrum of benzeneboronic anhydride

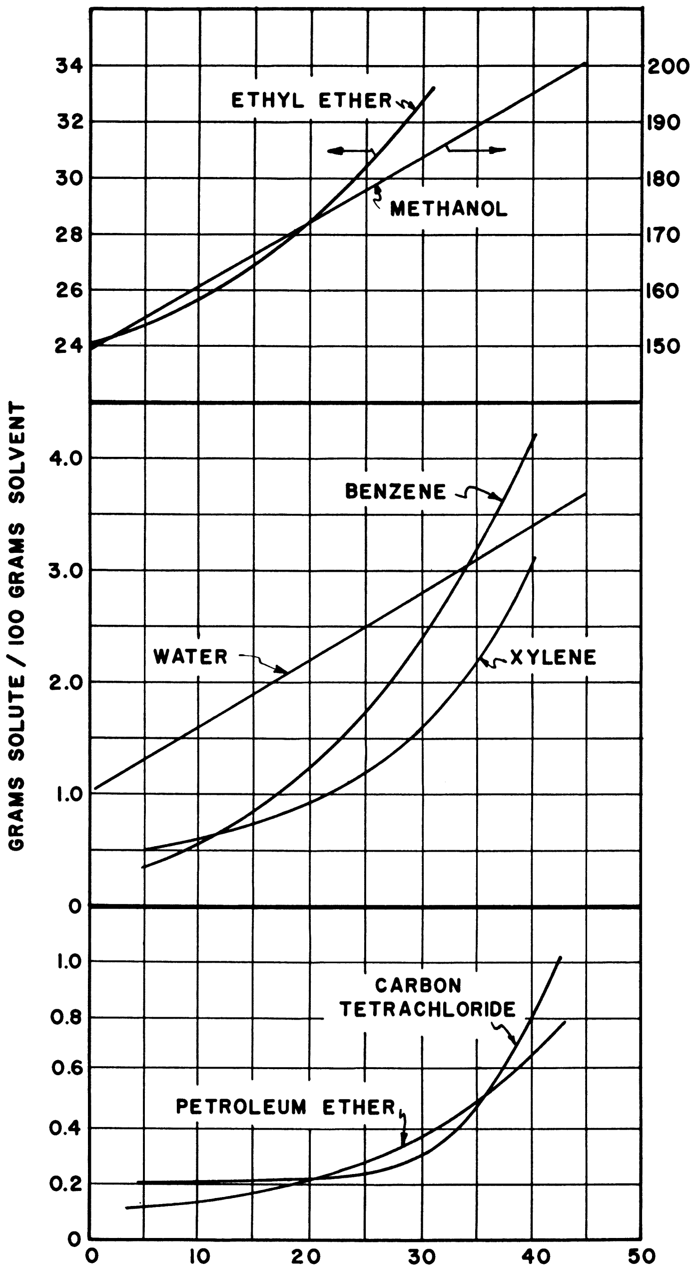


Figure 7. Solubility of benzeneboronic acid

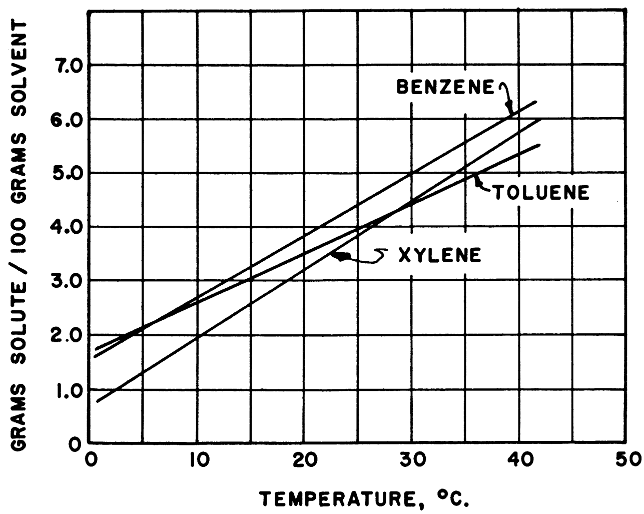
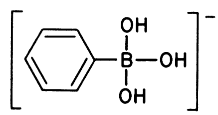


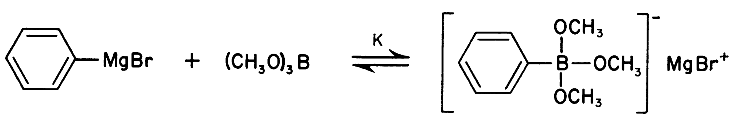
Figure 8. Solubility of benzeneboronic anhydride

There is, however, a large amount of evidence to indicate that a tetracoordinate boronate anion (Equation 8) and the equilibria in which it takes part are some of the most important aspects of the Grignard reaction. Kuivila and coworkers (*41–49*) have shown that a tetracoordinate boronate anion, II, is involved in the reaction of benzeneboronic acid and its derivatives with bromine (*43–45*), iodine (*49*), and hydrogen peroxide (*41, 42, 48*).



II

Many examples of boron compounds acting as Lewis acids are known. For example, sodium hydride and sodium methoxide react with methyl borate to give sodium trimethoxy- and sodium tetramethoxyborohydride, respectively (*14*). Then, by analogy, it might be expected that phenylmagnesium bromide would react with methyl borate according to Equation 8 to form a tetracoordinate complex.



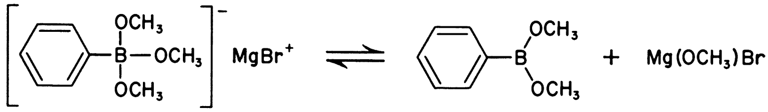
(8)

The reaction of phenylmagnesium bromide with methyl borate is highly exothermic, which probably results at least in part from a fast reaction rate. Further evidence for a fast reaction rate is afforded by the fact that the average yield of benzeneboronic acid for a slow rate of addition of Grignard reagent (3 moles/0.75 to 4.0 hours) is 46.8%, whereas the average yield for a fast rate of addition (3.0 moles/0.1 to 0.25 hour), followed by immediate hydrolysis, is 53.3%. Thus, the major part of the reaction must have occurred in a relatively short time. Furthermore, it can be assumed that K (Equation 8) is probably rather large, because, qualitatively, the heat liberated during hydrolysis of the reaction mixture (Equation 5) appears to be small

in comparison to the heat of hydrolysis of the Grignard reagent alone. This seems to indicate that most of the Grignard has reacted.

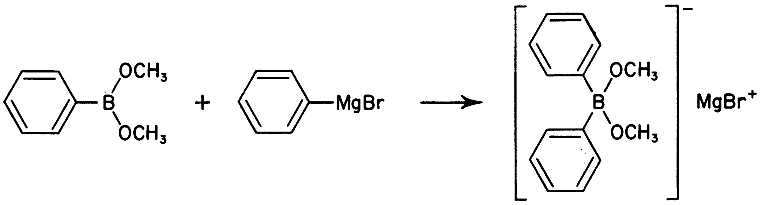
When phenylmagnesium bromide is added to an ethereal solution of methyl borate at low temperatures, and the reaction mixture is warmed to and stirred at 0°C. prior to hydrolysis, a much better yield is obtained than when the reaction proceeds at 0°C. followed by stirring and hydrolysis at 0°C. This suggested that some side reaction was occurring at higher reaction temperatures to limit the yield of benzeneboronic acid. A clue was afforded by the fact that the higher the reaction temperature, the higher the yield of dibenzeneborinic acid. Assuming that dibenzeneborinic acid could only result from the reaction of phenylmagnesium bromide with dimethyl benzeneboronate (Equation 10) various process variables and equilibria were considered which might lead to the formation of dimethyl benzeneboronate.

The boronate ester could arise by the thermal disproportionation of the tetracoordinate boronate anion of Equation 8, according to Equation 9.



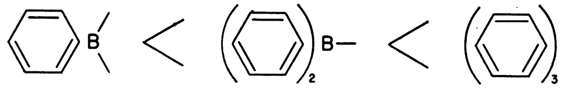
(9)

The effect of temperature then, can be at least partially interpreted in terms of Equation 9. As the temperature is increased, more dimethyl benzeneboronate is formed which in turn can compete with methyl borate for phenylmagnesium bromide (Equation 10).



(10)

The competing rates of reaction of phenylmagnesium bromide with methyl borate and dimethyl benzeneboronate will depend on a number of factors such as solubility of the two tetracoordinate complexes, relative Lewis acidity, and steric factors. In general, one would expect the diphenyl-substituted boron to be a better Lewis acid than the monophenyl compound, and hence, produce a more stable tetracoordinate complex which would provide a driving force for the formation of the diphenyltetracoordinate complex. For example, Letsinger and Skoog (*52*) have shown that dibutyl benzeneboronate forms a very unstable ammonia addition compound which decomposes at about 30°C., butyl dibenzeneborinate forms a more stable ammonia coordination compound which decomposes at about 64° to 67°C., and triphenyl borane forms a very stable coordination compound which decomposes at 170° to 176°C. Thus, the acidity of phenyl-substituted boron is in the order,

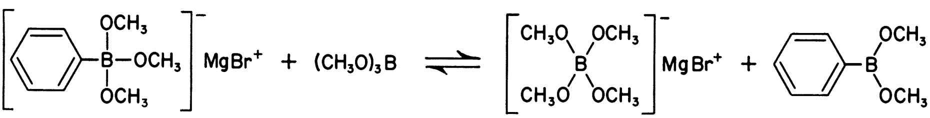


which is in accord with the observations of Johnson and Van Campen (*32*) for aliphatic boron compounds.

All workers prior to Seaman and Johnson (*71*) employed a "normal" Grignard reaction for the preparation of benzeneboronic acid, but Seaman and Johnson found that the yields were considerably improved by adding the Grignard reagent to the borate ester.

By adding the borate ester to the Grignard reagent, there was always an excess of phenylmagnesium bromide; this gave relatively large yields of borinic acid and correspondingly low yields of boronic acid. A consideration of Equation 10 shows that the presence of excess phenylmagnesium bromide can act as a driving force for the formation of the diphenyl complex from the monophenyl complex by removing dimethyl benzeneboronate as rapidly as it is formed. It was assumed above that formation of borinic acid occurred as a result of the formation and subsequent reaction of dimethyl benzeneboronate. The authors confirmed the effect of having excess phenylmagnesium bromide present by adding methyl borate to the Grignard. Under these conditions the yield of boronic acid was 42.8% and the yield of borinic acid, 39.9%. This can be compared to experiments in which the Grignard reagent was added to an ethereal solution of methyl borate under exactly comparable conditions yielding 53.3% of boronic acid and 18.2% of borinic acid (Table IV).

The inverse procedure of adding the Grignard reagent to the borate ester gives the condition of always having excess methyl borate present, which by mass action would be expected to reduce the effect of the reaction of phenylmagnesium bromide with dimethyl benzeneboronate. This is undoubtedly partly true. However, the acidity of methyl borate is well known, and a competitive equilibrium for the base, magnesium methoxybromide, $Mg(OCH_3)Br$, between dimethyl benzeneboronate and methyl borate would be expected (Equation 11).



(11)

Thus, an excess of methyl borate by mass action tends to drive Equation 8 to the right and tends to prevent formation of methyl dibenzeneborinate (Equation 10), but it also provides for the formation of dimethyl benzeneboronate.

This suggested that the reaction of a Grignard reagent with a borate ester should be conducted in such a manner that there would never be an excess of either borate ester or Grignard reagent; and if one of the two had to be in excess then it should be the ester.

The authors investigated this *a priori* conclusion by adding methyl borate and phenylmagnesium bromide in small stoichiometric increments to ether maintained at the desired temperature. Figure 7 gives the variation of yield with temperature using this method. At 0°C., a yield of 75.8% of boronic acid was obtained with only a trace of by-product borinic acid. This can be compared to an average run in which the Grignard reagent was added to the methyl borate at 0°C. yielding 53.3% of boronic acid and 18.2% of borinic acid. In both cases the reactants were added as rapidly as possible while a constant temperature was maintained.

Qualitatively, the authors concluded above that the equilibrium represented by Equation 8 is very rapidly attained. If the reaction were not reversible to some extent, the incremental run cited should have given a quantitative yield because no borinic acid was obtained. However, boron equivalent to 25% of unreacted methyl borate was found in the aqueous residue after extraction of the hydrolyzed reaction mixture. This also suggested the possibility that the secondary reactions involving formation of borinic acid and borane (resulting from excess methyl borate) act as a driving force to prevent, in effect, reversal of Equation 8 during the usual inverse Grignard reaction.

In one incremental run the reactants were added very slowly and the reaction mixture was stirred for about an hour before hydrolysis. In this case the yield of benzeneboronic acid was reduced to 63.5% with a concurrent formation of 28.2% of borinic acid. This further suggests that the rate of reaction leading to the mono-

phenyl tetracoordinate complex is much greater than the rate of formation of the diphenyl and triphenyl tetracoordinate complex (Equations 10 and 16).

There is, however, an anomaly here; when the incremental method is used at —60°C., followed by warming to, and hydrolysis at 0°C., a 99.5% yield of boronic acid was obtained (Table V and Figure 4, curve *D*). One would expect that the same equilibrium would be established on warming, so that regardless of the reaction temperature, some constant yield would be obtained. Apparently this is not the case. A number of possible explanations exist. The tetracoordinate complex might crystallize and the rate of solution be sufficiently slow to prevent reversal of the reaction within the experimental time allowed. Also, the reacting species has been assumed to be phenylmagnesium bromide. The Schlenk (*34*) equilibrium:

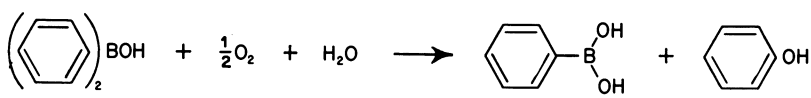
$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (12)$$

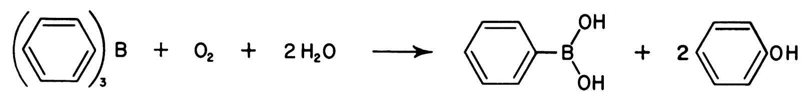
has not been considered in this discussion. For example, it is known that phenylmagnesium bromide 0.2178*N* in magnesium contains 31% of diphenylmagnesium at —15°C., and 35% at 35°C. This suggests the possibility that the reacting species is actually phenylmagnesium bromide, and a higher concentration of this would then be present at lower temperatures.

Unreacted Methyl Borate. Formation of Phenol, Benzene, and Dibenzeneborinic Acid. In all runs made at 0°C., boron equivalent to about 20% of unreacted methyl borate was found in the aqueous residue. The boron could arise in one of two ways and in varying amounts depending on the quantity of benzene formed. These products partially arise through hydrolysis (workup) of unreacted Grignard reagent (*27*) during the incremental method discussed above. However, during the addition of the Grignard reagent to methyl borate, the unreacted methyl borate and benzene probably arise, at least in part, as a result of other reactions described below.

The formation of dibenzeneborinic acid was discussed above as arising through the reaction of dimethyl benzeneboronate and phenylmagnesium bromide.

The small amounts of phenol observed during the high temperature runs probably did not result from oxidized Grignard reagent, as air was rigorously excluded from the reactants and apparatus. However, no precautions were taken to keep air out of the system during hydrolysis of the reaction mixture and subsequent extraction steps. The phenol might have been formed by the oxidation of either dibenzeneborinic acid (Equation 13) or more probably, by the oxidation of triphenyl borane with liberation of phenol upon subsequent hydrolysis (Equation 14).

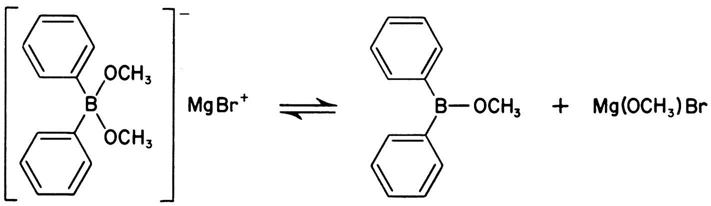

(13)


(14)

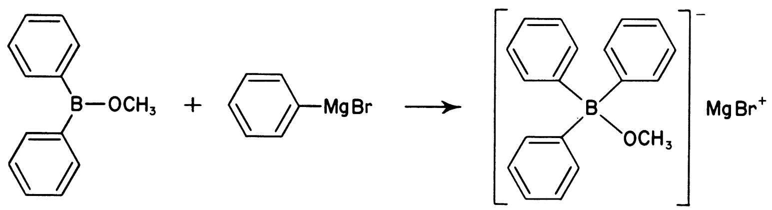
The fact that more phenol is apparently formed in the high temperature runs in which the yield of triphenyl borane would be higher, suggests that the oxidation of borane is the source of the phenol. Letsinger and Skoog (*52*) observed that a relatively large amount of triphenyl borane was obtained when the reaction of phenylmagnesium bromide and isobutyl borate proceeded at reflux, but only a small quantity was obtained at a reaction temperature of —70°C.

As triphenyl borane reacts with hot water, the presence of borane could also account for at least part of the benzene obtained (Equation 17).

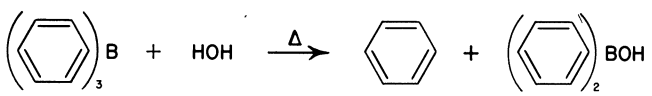
Torssell (*79*) (Equation 16) has shown that the esters of borinic acids react with Grignard reagents to form boranes. If one assumes again that there must be an initial dissociation of the diphenyl-tetracoordinate complex (Equation 15) then the arguments given above for dimethyl benzeneboronate would hold here also.



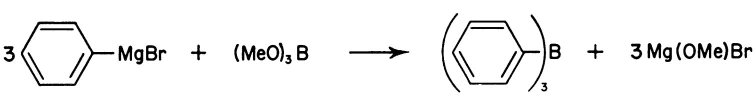
(15)



(16)



(17)



(18)

The over-all equation for the formation of triphenyl borane (Equation 18) indicates that 3 moles of phenylmagnesium bromide react with 1 mole of methyl borate. However, the reactants are mixed in a 1 to 1 molar ratio for the formation of benzeneboronic acid. Thus, if there is any borinic acid or borane formed, then there will be unreacted methyl borate at the end of the reaction, and when the reaction mixture is hydrolyzed, and neutralized, methyl borate equivalent to the borinic acid and borane formed is hydrolyzed to methanol and boric acid.

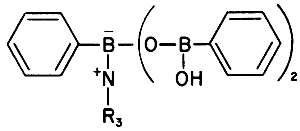
Dibenzeneborinic acid is probably stable under the hydrolysis and neutralization conditions used. Therefore, at least part of the benzene probably arises through the cleavage of triphenyl borane to yield dibenzeneborinic acid and benzene (Equation 17). This is significant, because triphenyl borane, which is known to be formed at higher temperatures but which would not be observed or isolated under the experimental conditions, could account for at least part of the benzene, phenol, and boric acid equivalent to unreacted methyl borate. As was pointed out above, the Lewis acidity and hence the stability of the tetracoordinate boronate anion probably increase with the number of phenyl groups. Thus, the equilibria (Equations 10 and 16) are probably not reversible to any great extent, and once conditions arise which promote the formation of trivalent boron compounds such as dimethyl benzeneboronate (Equation 9) and methyl dibenzeneborinate (Equation 15), the yield of boronic acid is limited.

A study of the steric effects and electronic effects on the formation and stability of the tetracoordinate boronate anion (I) will be reported in a subsequent publication.

Reactions and Uses of Benzeneboronic Acid

Benzeneboronic acid is such a versatile chemical intermediate that a brief discussion of the products that can be derived from it is in order. More general information about organoboron chemistry can be found in a recent review by Lappert (*50*).

Branch and Yabroff (*7*, *87*) found that benzeneboronic acid formed crystalline amine adducts (III) with diethylamine, triethylamine, propylamine, pyridine, and piperidine.



III

They found that acetonitrile, benzonitrile, phenylacetonitrile, aniline, diphenylamine, acetic anhydride, and sodium acetylacetonate did not form stable addition compounds with benzeneboronic acid.

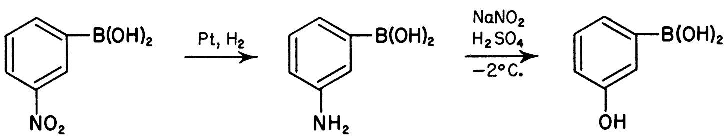
Dehydration. Benzeneboronic acid is easily dehydrated to the anhydride. The reaction was discussed above.

Nitration. The nitration of benzeneboronic acid was first reported by Ainley and Challenger (*2*). With sulfuric-nitric acids above −10°C. they observed considerable charring, but at −20°C. a 70% yield of *m*-nitrobenzeneboronic acid was obtained. Seaman and Johnson (*71*) found that nitration with fuming nitric acid at −15°C. gave 70% of *m*-nitro- and 10% of *o*-nitrobenzeneboronic acid, but nitration with excess fuming nitric acid in acetic anhydride at −15°C. gave 60% of *o*-nitro- and 2% of *p*-nitrobenzeneboronic acid. A small amount of nitrobenzene was always formed, and at higher temperatures, nitrobenzene and boric acid were the sole products.

Reduction of Nitrobenzeneboronic Acids. Seaman and Johnson (*71*) obtained 44 to 48% yields of *m*-aminobenzeneboronic acid by reduction of the nitro compound with ferrous hydroxide. Attempts to isolate the *o*-amino compound or its acetyl derivative yielded benzeneboronic acid instead; however, the benzoyl derivative was isolated in 37% yield from the reaction mixture. Subsequently, Bean and Johnson (*3*) obtained *m*-amino- and *o*-aminobenzeneboronic acid in 85 to 90 and 24% yields, respectively, by catalytic reduction of the nitro compounds.

Snyder and Weaver (*74*) have reported the preparation and *in situ* use of *m*-diethylaminobenzeneboronic acid by reduction of the nitro compound in the presence of acetaldehyde.

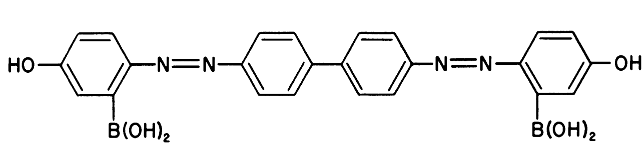
Diazotization of Aminobenzeneboronic Acid. Bean and Johnson (*3*) reported the preparation of *m*-hydroxybenzeneboronic acid in an over-all yield of 30% based on *m*-nitrobenzeneboronic acid (Equation 19).



(19)

The *m*-hydroxy compound has also been prepared by Snyder and his coworkers (*73–76*).

Diazo-coupling Reactions of *m*-Hydroxy-, *m*-Amino-, and *m*-Diethylaminobenzeneboronic Acids. Snyder and his coworkers (*73–76*) have prepared a number of very interesting compounds using *m*-hydroxy-, *m*-amino-, and *m*-diethylaminobenzeneboronic acid as starting materials. In all cases the boronic acid couples para to the amino or hydroxy function. For example, addition of benzidine tetrazonium chloride solution to *m*-hydroxybenzeneboronic acid gave 4,4′-bis-(2-borono-4-hydroxybenzeneazo)-biphenyl (IV) in 69% yield.



IV

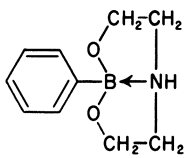
Many other examples of this coupling reaction are given by Snyder and coworkers (*73–76*).

Kuivila (*43*) reported that *m*-iodobenzeneboronic acid could not be prepared from the diazonium salt and cuprous iodide. This confirms the findings of Snyder and coworkers and Ainley and Challenger (*2*) that cuprous salts cause cleavage of the boron-carbon bond.

Esterification of Benzeneboronic Acid and Reactions of Boronate Esters. Esters of benzeneboronic acid were obtained by Khotinsky and Melamed (*35*) in unstated yields as intermediates in the preparation of benzeneboronic acid from phenylmagnesium bromide and borate esters. However, Brindley, Gerrard, and Lappert (*9*) found this procedure unsatisfactory. They preferred to esterify the boronic acid or anhydride by removing water of reaction by azeotropic distillation. The azeotropic procedure of Dupire (*24*) was used by Torssell (*79–81*) for the preparation of dimethyl benzeneboronate.

Di-*tert*-butyl benzeneboronate was best prepared from benzeneboronyl dichloride and *tert*-butyl alcohol in the presence of pyridine (*9, 11*). Esters of benzeneboronic acid generally undergo facile hydrolysis and alcoholysis with higher alcohols. Both reactions apparently involve cleavage of a boron-oxygen bond, because hydrolysis of di-(+)-2-methylheptyl benzeneboronate afforded (+)-2-octanol. Also, neopentyl alcohol was recovered unchanged from the hydrolysis of dineopentyl benzeneboronate (*11*) [cf. Scattergood, Miller, and Gammon (*67*)].

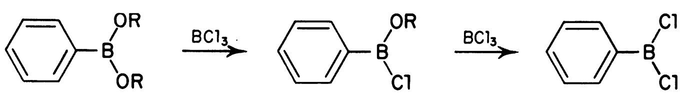
The diethanolamine ester of benzeneboronic acid (V) is not hydrolyzed by water (*52, 62*). This probably results from the coordination of the amine nitrogen with boron [cf. Brown and Fletcher (*13*)].



V

Esters of benzeneboronic acid react with Grignard reagents to give excellent yields of unsymmetrical diareneborinates (*51, 53, 79, 80*).

Brindley, Gerrard, and Lappert (*10*) have discussed the reaction of boronate esters with boron and hydrogen halides. In general, boron halides react with boronate esters according to Equation 20.

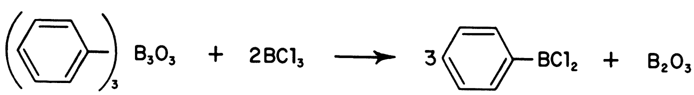


(20)

The reaction of hydrogen bromide with di-(+)-2-methylheptyl benzeneboronate gave (−)-2-bromo-octane.

Kuivila, Keough, and Soboczenski (*46*) prepared esters of benzeneboronic acid and polyhydroxy compounds in 57 to 96% yields by mixing hot saturated solutions of mannitol, sorbitol, catechol, pinacol, pentaerythritol, diethyl-D-tartrate, and *cis*-indan-1,2-diol, and the boronic acid.

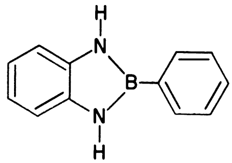
Conversion of Benzeneboronic Acid to Benzeneboronyl Dichloride. Schupp and Brown (*70*) reported the preparation of benzeneboronyl dichloride in approximately 50% yields from the reaction of boron trichloride and benzeneboronic acid anhydride (Equation 21).



(21)

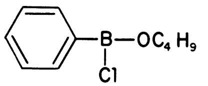
This reaction has also been investigated by Abel, Dandegaonker, Gerrard, and Lappert (*1*) who found that boron trifluoride did not react analogously.

Schupp and Brown (*70*) proposed the structural formula VI for the reaction product of benzeneboronyl dichloride and *o*-phenylenediamine.



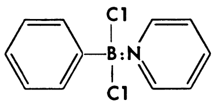
VI

Brindley, Gerrard, and Lappert (*11*) have shown that benzeneboronyl dichloride reacts with alcohols to give intermediate products exemplified by VII.



VII

These authors also reported a stable complex (VIII) formed between pyridine and benzeneboronyl dichloride.



VIII

Cleavage of the Boron-Carbon Bond in Benzeneboronic Acid. Michaelis and Becker (*58*) observed that phenylmercuric chloride was obtained when benzeneboronic acid was treated with an aqueous solution of mercuric chloride. This reaction also proceeds with the bromide (*2*) and has been used for the analysis of boron compounds (*29, 30, 35, 38*) and mercury compounds (*86*).

Holzbecher (*29, 30*) has shown that a quantitative yield of diphenyl mercury was obtained from the reaction of benzeneboronic acid and aqueous mercuric nitrate in the presence of sodium acetate and that a quantitative yield of phenylmercuric iodide was obtained when the reaction was allowed to proceed in the presence of potassium iodide, ammonium nitrate, and ammonia.

Challenger and Parker (*22*) found that thallic chloride and bromide react in hot aqueous solution with benzeneboronic acid, yielding, according to the proportion of boronic acid used, mono- or diphenylthallium halides. These results were confirmed by Mel'nikov and Robitskaya (*57*).

Michaelis and Becker (*59*) reported the formation of a "silver mirror" and benzene when benzeneboronic acid was warmed with ammoniacal silver nitrate. Seaman and Johnson (*71*) and Bean and Johnson (*3*) used the reaction to remove the boronic acid group for purposes of identifying substituted benzeneboronic acids. The reaction was formulated not as a reduction but as a hydrolytic cleavage (Equation 22). The hydrolytic cleavage has been confirmed (*33*).

$$C_6H_5B(OH)_2 + H_2O \xrightarrow{Ag(NH_3)^+} C_6H_6 + H_3BO_3 \tag{22}$$

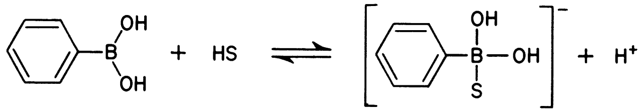
Ainley and Challenger (*2*) investigated a number of cleavage reactions of benzeneboronic acid. The boronic acid was found to react readily with chlorine or bromine water to give chloro- or bromobenzene (Equations 23 and 24).

$$C_6H_5B(OH)_2 + Cl_2 + HOH \rightarrow C_6H_5Cl + HCl + H_3BO_3 \tag{23}$$

$$C_6H_5B(OH)_2 + Br_2 + HOH \rightarrow C_6H_5Br + HBr + H_3BO_3 \tag{24}$$

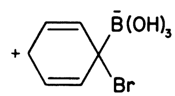
The reaction with bromine water has been used as a rapid method for determining boron in aromatic organoboron compounds; the results are said to be accurate to within 0.1% boron (*56*).

The electrophilic displacement of the boronic acid group has been investigated kinetically in a series of excellent papers by Kuivila and his coworkers (*43–45, 47*). They have shown that the mechanism involves the rapid and reversible formation of a tetracoordinate boronate anion (II) from benzeneboronic acid and solvent, HS, which



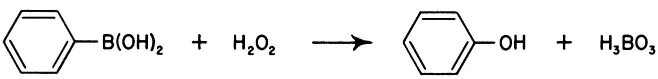
II

then reacts with molecular bromine by way of the discrete intermediate IX in the rate-determining step.



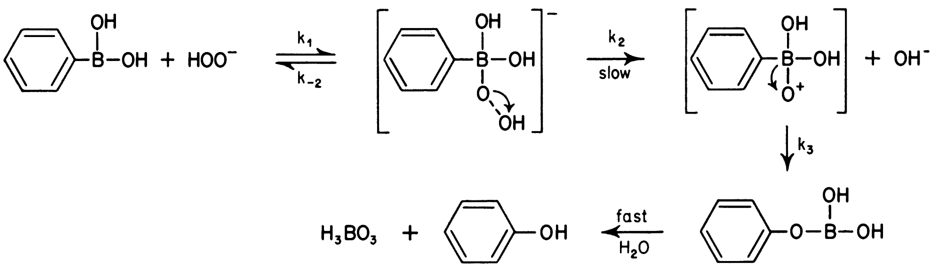
IX

Iodine in excess potassium hydroxide reacts with benzeneboronic acid to give iodobenzene (*2*, see also *49*). Phenol and boric acid are obtained from the reaction of benzeneboronic acid and aqueous hydrogen peroxide (Equation 25) (*2, 41, 42, 48, 55*).

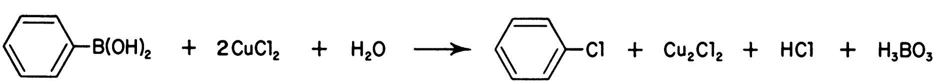


(25)

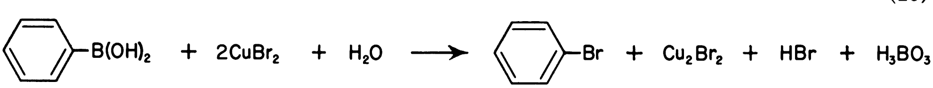
The kinetics (*41, 42, 48*) for this reaction indicate that there are two ionic mechanisms acting: both are first order in peroxide; one is first order and the other is second order in boronic acid. The reaction is catalyzed by many polyhydroxy compounds, exhibits a positive salt effect, and has the characteristics of first-order specific lyate ion catalysis. These facts are satisfied by the following mechanism:



Hot aqueous solutions of cupric chloride and bromide react with benzeneboronic acid to give good yields of chloro- and bromobenzene (Equations 26 and 27), whereas



(26)

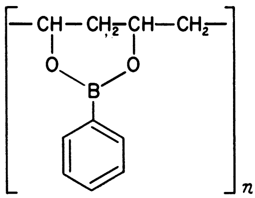


(27)

hot aqueous cupric sulfate gives benzene, diphenyl, and phenol (*2*). Benzonitrile is obtained in low yield from a hot mixture of cupric sulfate, potassium cyanide, and benzeneboronic acid.

Water at 140°C. for 40 hours or hot 50% sodium hydroxide was found to cleave benzeneboronic acid yielding benzene (*2*). The reaction of benzeneboronic acid with water is catalyzed by zinc and cadmium halides. Beryllium, magnesium, and calcium salts do not react (*2*).

Formation of Polymers from Benzeneboronic Acid. Salzberg and Signaigo (*66*) have described polymers formed from high viscosity poly(vinyl alcohol) and benzeneboronic acid having the probable structure X.

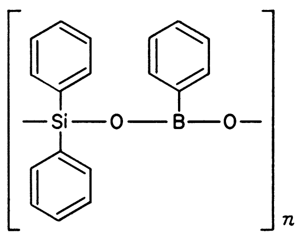


X

The films made from this material are said to be very tough.

Aqueous dispersions of poly(vinyl borate) formed by mixing dilute poly(vinyl alcohol) with boric acid solution, react in the same way toward iodine as do amylose solutions by giving a strong absorption band at 670 mμ. Under similar conditions, poly(vinyl benzeneboronate) dispersion does not give a color reaction (*85*).

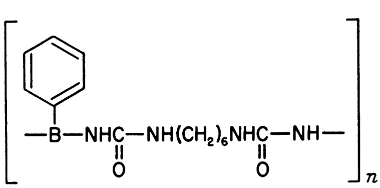
Upson (*83*) has described polymeric products derived from diphenylsilane and benzeneboronic acid, having the proposed structure XI. These materials are



XI

said to give clear, transparent films and can be drawn into fibers. A similar material has been described by Hizawa and Nojimoto (*28*). It was claimed to give an electrically insulating film when baked on a copper plate.

Upson (*82, 84*) has also described polymeric *N*-boroureas (XII) prepared from hexamethylene diureas and *N*-boroamides derived from hexamethylene diisocyanates and benzeneboronic acid.



XII

Miscellaneous Uses of Benzeneboronic Acid. It has been claimed (*54*) that di-(carboethoxyundecyl)-benzeneboronate greatly improves film strength and extreme pressure characteristics of lubricating oils.

Michaelis and Becker (*58, 59*) reported that benzeneboronic acid was toxic toward microorganisms and relatively nontoxic toward higher animals.

Seaman and Johnson (*71*) and Bean and Johnson (*3*) investigated the bacteriostatic effects of a number of areneboronic acids upon *Staphylococcus aureus.* In general, benzeneboronic acid was found to be only slightly effective, but Brown and coworkers (*12*) considered benzeneboronic acid as highly toxic. They tested a number of compounds against laboratory-reared larvae of the housefly (*M. domestica*), the confused flour beetle (*T. confusum*), the Mediterranean flour moth (*E. Kuehniella*), and adults of the granery weevil (*S. granarius*). These results were:

Musca		Sitophilus		Tribolium		Ephestia	
LC_{50}	LC_{90}	LC_{50}	LC_{90}	LC_{50}	LC_{90}	LC_{50}	LC_{90}
700	1450	102	305	50	450	150	270

Beran, Prey, and Böhm (*4*) also found benzeneboronic acid to be a good insecticide when tested against *Calandra granaria, Tenebrio molitor, Musca domestica,* and *Carausius morosus.*

Benzeneboronic acid has bacteriostatic action equal to phenol when tested against *Staphylococcus aureus* (cf. *3*) and *Escherichia coli* while the bactericidal action is less than phenol (*20*). The sodium salt of benzeneboronic acid is said to be a poison to the respiratory system, but does not affect the heart (*19*). The lethal dose of the sodium salf for dogs was 0.4 gram per kg. weight (*21*). The lethal dose of the acid was reported as 560 mg. per kg. intraperitoneally in the mouse and 284 mg. per kg. in the guinea pig. The intravenous lethal dose in the dog was 450 mg. per kg. (*21*).

Caujolle and his coworkers have also found that benzeneboronic acid has a definite effect on the germination of seeds and on the root growth of plants (*15–18*).

Acknowledgment

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Preparation, Properties, and Uses of Borate Esters

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The esters of orthoboric acid, although known for more than 100 years (58), have only recently become commercially available. This paper presents process development data; the synthesis and properties of a new series of hydrolytically stable borates; the variation in boiling point, density, index of refraction, and viscosity with temperature; a summary of reactions and uses; and physical evidence that tetracoordinate boron is involved in the reactions of borate esters.

A number of methods for preparing borate esters have been described. They include: reaction of an alcohol (or phenol) with boron trichloride (*48, 134*) (Equation 1); boron acetate (*3, 146*) (Equation 2); boric acid (*47, 149*) (Equation 3); boron oxide (*188*) (Equation 4); or sodium borohydride (*36*) (Equation 5); and trans-esterification with a lower boiling borate ester (*170, 204*) (Equation 6). When water is a product of the esterification, it has been removed by azeotropic distillation with an excess of the alcohol (*14, 92, 164*) or an inert medium (*149*); or by dehydration with sulfuric acid (*45, 197*), copper sulfate (*56, 93*), or boron oxide (*120, 126, 172, 197*) (Equation 7).

$$3ROH + BCl_3 \rightarrow (RO)_3B + 3HCl \quad (1)$$

$$6ROH + (CH_3COO)_4B_2O \rightarrow 2(RO)_3B + 4CH_3COOH + H_2O \quad (2)$$

$$3ROH + H_3BO_3 \rightarrow (RO)_3B + 3H_2O \quad (3)$$

$$6ROH + B_2O_3 \rightarrow 2(RO)_3B + 3H_2O \quad (4)$$

$$3ROH + NaBH_4 + H^+ \rightarrow (RO)_3B + 4H_2 + Na^+ \quad (5)$$

$$3ROH + (R'O)_3B \rightarrow 3(RO)_3B + 3R'OH \quad (6)$$

$$3ROH + B_2O_3 \rightarrow (RO)_3B + H_3BO_3 \quad (7)$$

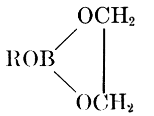
Stanley (*180*) has claimed the preparation of borate esters as an intermediate step in the conversion of alkylenes into alcohols. The alkylene is converted to the alkyl sulfate, alkyl phosphate, or alkaryl sulfonate by absorption into acid or acid ester; the borate ester formed on subsequent reaction with boric acid is then distilled and hydrolyzed to the alcohol:

$$3SO_2(OEt)_2 + H_3BO_3 \rightarrow 3SO_2(OEt)OH + (EtO)_3B \xrightarrow{H_3BO_3} 3H_2SO_4 + (EtO)_3B \quad (8)$$

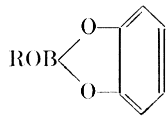
Barnes and coworkers (*15*) recently claimed the production of methyl, ethyl, propyl, and butyl borates by reaction of boron trifluoride etherate with the alcohol and sodium alcoholate:

$$BF_3:O(C_2H_5)_2 + 3NaOCH_3 + CH_3OH \rightarrow \underset{\text{azeotrope}}{[B(OCH_3)_3 + CH_3OH]} + 3NaF + (C_2H_5)_2O \quad (9)$$

In general, attempts to prepare mixed borate esters of monohydroxy compounds result in disproportionation to the corresponding symmetrical esters (*47, 48, 170, 188*). Mixed esters have, however, been synthesized by use of a polyhydric alcohol (ethylene glycol) or phenol (catechol) in conjunction with a monoalcohol to give the cyclic products, I and II (*118, 188*):

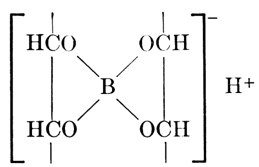


I



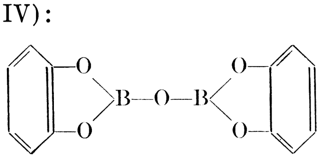
II

The simple borates of polyhydric alcohols have been described (*3, 49, 146, 151, 170*). The effectiveness of certain polyhydric alcohols (mannitol, glycerol) used in the standard alkaline titration of boric acid has been attributed by Böeseken (*23, 26, 27*) to the formation in water of strong acids in which the esterified boron atom has become tetracoordinate (III):



III

The tetrahedral structure of boron in esters of *cis*-dihydroxy compounds was established by resolution of boron bis-(γ-chlorocatechol) and of boron bis-(3-nitrocatechol), each into two optically active forms. Similarly, the borosalicylate ion and the α-hydroxybutyrate derivative were found to be optically active (*23–25*). On the other hand, catechol borate, prepared by melting together catechol and boron oxide, was assigned the structure (IV):



IV

Although the ester is hydrolyzed by water, the salts are stable (*165–167*). This suggests that borates having trigonal coplanar boron are formed under anhydrous conditions, while borates having tetrahedral boron as the center of symmetry result when water is present.

The unusually high resistance to hydrolysis of the alkanolamine borates and aminoethyl diarylborinates has been attributed to the tetrahedral configuration of boron in a tryptich structure resulting from the transannular coordination of a pair of electrons on the nitrogen atom with the open sextet on the boron (*35, 62, 119, 181*). That triisopropanolamine borate is considerably more hydrolysis-resistant than triethanolamine borate (*181*) may result from the additional steric effect in the former.

The polyfunctionality of boric acid (or boron oxide) and the polyhydroxy compounds readily leads to the formation of condensation polymers and copolymers. Several patents describing such materials are listed in Table XIX.

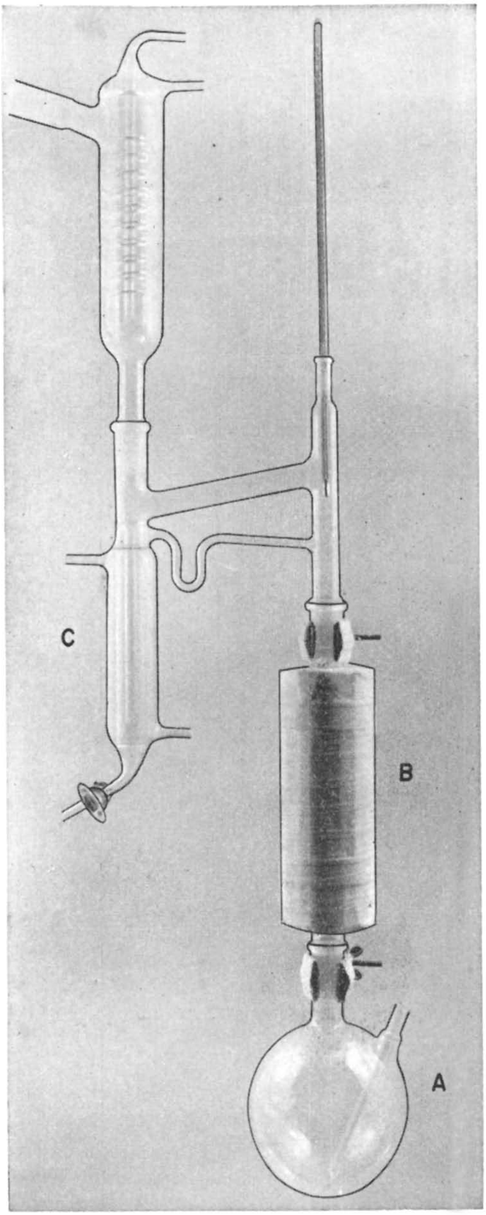


Figure 1. Apparatus for laboratory study of azeotropic distillation method

A. 1-liter flask
B. Vigreux column
C. Water-cooled azeotrope decanter

The only partially esterified boric acid [$ROB(OH)_2$] which has been reported is 1-methyl boric acid (*142*). Scattergood, Miller, and Gammon (*164*) and Steinberg and Hunter (*181*) have suggested that the partially esterified boric acids occur as intermediates in the stepwise hydrolysis of the fully esterified compounds. Gerrard

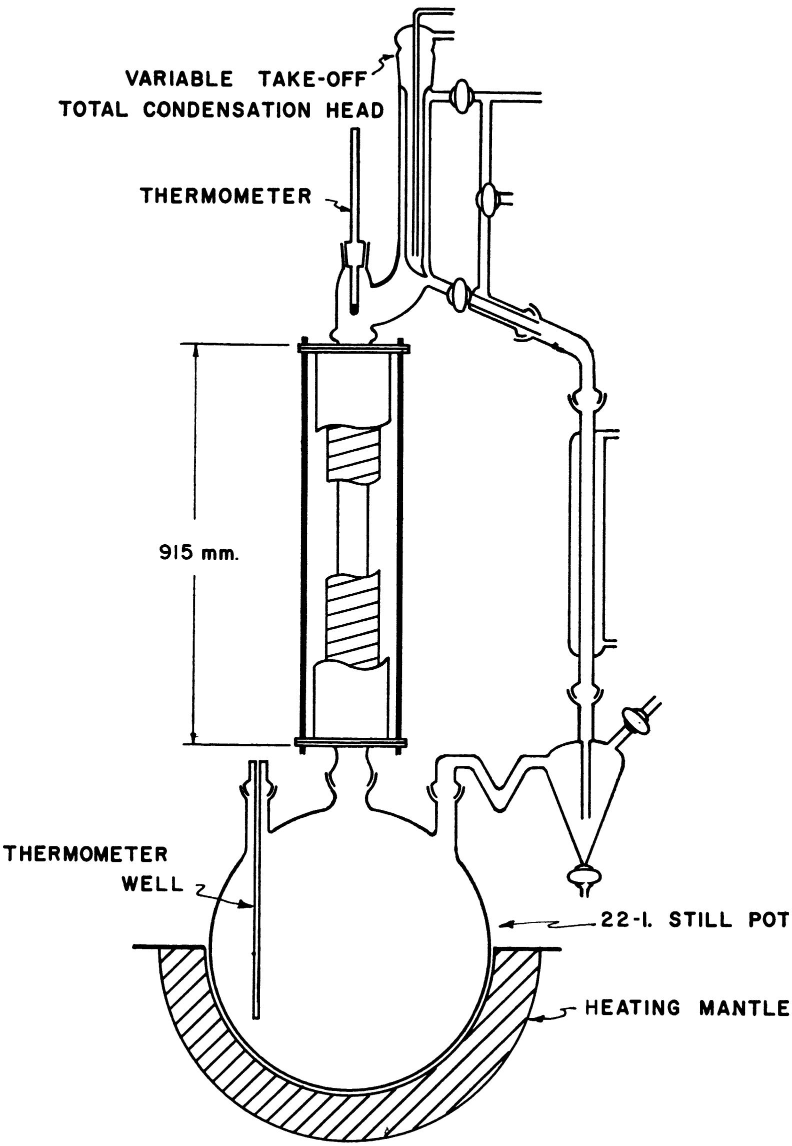


Figure 2. Apparatus for large-scale laboratory azeotropic distillation

and Lappert (*73*) postulated a similar mechanism for the dealkylation of the triesters by hydrogen halides, although no evidence for the intermediate dealkylated forms was found. The magnesium, aluminum, calcium, barium, tin, and chromium salts of many mono- and disubstituted alkoxy and aryloxy boric acids have been claimed in patents (*44*, *54*).

Process Development

In developing processes for the manufacture of various borate esters, the authors have used azeotropic distillation (Method I, Equations 3 and 4); transesterification

(Method II, Equation 6); or dehydration with boron oxide (Method III, Equation 7).

The relative efficiencies in Method I of boric acid *vs.* boron oxide and of a variety of azeotropic media were investigated in a series of standard experiments using the apparatus shown in Figure 1. The water-cooled trap (designed by the authors; constructed by Stanford Glassblowing Laboratories, Palo Alto, Calif.) was much more satisfactory for separating the azeotropes than the commonly used Dean-Stark trap. The alcohol (used as received) and the stoichiometric amount of boron compound (boric acid or boron oxide) were heated at a constant power input selected to give a moderate boil-up rate (219 watts). An equal weight of reactants (500 grams) was used in each case. The reaction was followed by measuring the amount of water collected in the trap, and was terminated when approximately the theoretical amount had been removed. The ester was purified by stripping the azeotropic medium at atmospheric pressure, removing any unreacted alcohol under moderate vacuum (aspirator), then distilling through a short Vigreux or packed column at about 5 mm. (methyl and ethyl borate form azeotropes; isopropyl borate requires efficient fractionation to obtain good separation from the alcohol). Larger-scale laboratory preparations were conducted in the apparatus shown in Figure 2.

Typical curves of the progress of the standard reactions are given in Figure 3. The rate of formation is taken as the slope of the least squares line calculated for the initial linear portion of the plot of ester formed (based on water collected) *vs.* reaction time. Mono-olefins (Table I) give faster rates of ester formation of the aliphatic

Table I. Comparison of Effect of Azeotropic Medium on Rate of Ester Formation

(Standard reaction with B_2O_3)

Azeotropic Medium	Weight % H_2O in Binary Azeotrope[a]	Rate, Moles/Hour: *n*-Butyl borate	Rate, Moles/Hour: *n*-Dodecyl borate
1-Butanol[b]	42.5	1.12	—
1-Dodecanol[c]	—	—	1.56
Benzene[d]	8.83	2.21	1.45
Xylene[e]	35.8	—	1.47
Diisobutylene[f]	13.0	2.56	2.16
1-Octene[g]	34.7	2.78	2.01
Tripropylene[h]	28.6	2.58	1.74
Tetrapropylene[i]	66.0	2.48	1.74

[a] Azeotrope data for butanol, benzene, and xylene from (*87*).
[b] Union Carbide Chemicals Corp.
[c] Aceto Chemical Co.
[d] Baker and Adamson.
[e] Phillips Petroleum Co.; mixture of meta- and para-isomers.
[f] Atlantic Refining Co.; approximately 4:1 mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.
[g] Matheson, Coleman and Bell.
[h] Enjay Co.; mixture of mono-olefins: 33 vol. % C_8, 50 vol. % C_9, 17 vol. % C_{10}.
[i] Enjay Co.; mixture of mono-olefins.

borates than does an excess of the alcohol or the common aromatic azeotropic media; boron oxide (Table II) reacts faster than boric acid. For aromatic borates, the mono-olefins are also more effective, although here boric acid seems to be a better boron source than boron oxide.

Table I shows that the higher efficiency of the olefins relative to the other media is not related to the amount of water in the corresponding binary azeotrope. Although the matter was not studied in detail, a brief investigation of the minimum-boiling ternary azeotrope, diisobutylene-butanol-water (Table III), demonstrated that a substantial amount of the alcohol is carried over; the olefin and alcohol are, of course, returned to the system when the cooled distillate is decanted. The composition of the ternary azeotrope was obtained by distillation of a mixture of the components, removal of water from the total distillate with potassium carbonate, and infrared analysis of the organic layer. The amount of water remaining in the organic layer was found by Karl Fischer titration.

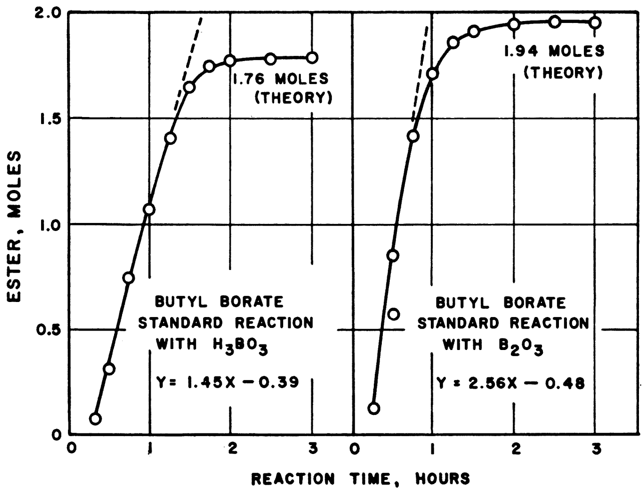


Figure 3. Comparison of rates of *n*-butyl borate formation with boron oxide and boric acid by azeotropic distillation

A comparison was also made, on a 1-liter scale, of the azeotropic distillation (Method I) and transesterification (Method II) processes for the preparation of a technical grade of the aliphatic borates. The compounds included in the comparison were the *n*-butyl, cyclohexyl, 2-ethylhexyl, 2,6,8-trimethyl-4-nonyl, and 2-methyl-7-

Table II. Comparison of Effect of Boron Oxide and Boric Acid on Rate of Ester Formation

(Standard reaction with diisobutylene)

Alcohol	Alcohol, Moles	Boron Compound, Moles	Rate, Moles/Hour B_2O_3[a]	Rate, Moles/Hour H_3BO_3[a]
1-Butanol[b]	5.83	0.971	2.56	—
	5.27	1.76	—	1.45
2-Ethylhexanol[b]	3.52	0.586	2.57	—
	3.31	1.10	—	1.75
2-Methyl-2 pentanol[b]	4.39	0.731	2.03	—
	4.07	1.36	—	1.50
2-Methyl-7-ethyl-4-undecanol[b]	2.20	0.367	1.88	—
	2.12	0.708	—	1.18
1-Dodecanol[c]	2.52	0.420	2.16	—
	2.41	0.804	—	1.30

[a] American Potash & Chemical Corp.
[b] Union Carbide Chemicals Corp.
[c] Aceto Chemical Co.

ethyl-4-undecyl borates. In the azeotropic distillation study, diisobutylene was used as the inert medium; in the transesterification experiment, isopropyl borate was used as the exchange ester. For both sets of experiments, the apparatus was similar to that shown in Figure 1, except that the flask had an extra neck for the withdrawal of

Table III. Composition of Diisobutylene-Butanol-Water Azeotrope

Phase	Weight % Water	Weight % 1-Butanol	Weight % Diisobutylene	Weight % Total
Organic	0.3	9.2	77.9	87.4
Water	12.3	0.3	—	12.6
Azeotrope	12.6	9.5	77.9	100.0

samples and a column (45 × 2.54 cm.) packed with 0.24-inch protruded stainless steel packing (Scientific Development Corp., State College, Pa.) was used. In the transesterification experiments the azeotrope trap was replaced by a Whitmore-Lux column head (*202*) manually set at a reflux ratio of approximately 4 to 1.

When the reactions were completed, as indicated by collection of approximately the theoretical amount of water or 2-propanol, the column was replaced by a Claisen head and ice-cooled receiver, and the reaction mixture was stripped at atmospheric pressure to a maximum of 250°C. Samples were withdrawn from the pot at intervals without interrupting the distillation. The same procedure was then repeated on each reaction mixture at 20 and 5 mm. Typical data relating to the boron and alcohol content to the stripping operation are shown for butyl borate in Table IV.

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Table IV. Relation of Boron and Alcohol Content of Tri(*n*-butyl) Borate to Stripping Temperature at Atmospheric Pressure

Pot Temp., °C.	Boron, %	Alcohol, %	Ester, % (on Boron)
	Azeotropic Distillation Method		
125	3.11	21.8	66.2
130	3.51	20.4	74.7
150	4.28	7.7	91.1
175	4.48	3.5	95.3
200	4.55	2.5	96.8
225	4.63	0.9	98.5
235	4.66	0.3	99.2
	Transesterification Method		
175	4.55	5.2	96.8
200	4.57	2.4	97.2
225	4.66	1.4	99.2
250	4.68	0.1	99.6

On the basis of the information thus obtained, a new run was made for each ester under process conditions selected to provide products of high purity in good yield. With butyl borate as an example, the stoichiometry and reaction conditions and material balances for the two methods being compared are shown in Tables V, VI, and VII. A summary of the results obtained with the various esters by both preparative methods is given in Table VIII.

Table V. Stoichiometry and Reaction Conditions for Preparation of Tri(*n*-butyl) Borate by Azeotropic Distillation under Selected Conditions

Reactants	
Alcohol, grams	185.30 (2.5 moles)
Boron oxide, grams	29.25 (0.42 mole)
Water removed	
Pot temp., °C.	99–114
Head temp., °C.	81–98
Heating time to remove water, hr.	0.33
Water removed, ml. (theory 22.7)	22.2
Azeotropic medium recovered (diisobutylene)	
Pot temp., °C.	113–122
Head temp., °C.	100–107
Pressure, mm. Hg	760
Heating time, hr.	0.2
DIB recovered, ml.	176
Boron, %	0.06
Products	
Pot temp., °C. (sampled)	227
Pressure, mm. Hg	760
Boron, % (theory 4.70)	4.67
Alcohol, %	2.8
Total heating time for reaction, hr.	1.33
Yield	
grams (theory 191.7)	190
%	99.1
Purity (% ester)	
Based on boron content	99.4
Based on alcohol content	97.2

Table VI. Stoichiometry and Reaction Conditions for Preparation of Tri(*n*-butyl) Borate by Transesterification under Selected Conditions

Reactants	
Alcohol, grams	185.30 (2.5 moles)
Isopropyl borate, grams	156.66 (0.83 mole)
Alcohol removed	
Pot temp., °C.	103–126
Head temp., °C.	81–106
Heating time to remove alcohol, hr.	0.75
Alcohol removed	
Ml. (theory 191.4)	193
Grams	150.1
Boron, %	0.02
Products	
Pot temp., °C. (sampled)	232
Pressure, mm. Hg	760
Boron, % (theory 4.70)	4.69
Alcohol, %	0.55
Total heating time for reaction, hr.	3.27
Yield	
Grams (theory 191.7)	189.2
%	98.7
Purity (% ester)	
Based on boron content	99.8
Based on alcohol content	99.4

Table VII. Materials Balance for Preparation of Tri(*n*-butyl) Borate

	Azeotropic Distillation[a]	Transesterification[b]
Materials in, grams		
Alcohol	185.30	185.30
Boron oxide	29.25	—
Diisobutylene	128.00	—
Isopropyl borate	—	156.66
Total	243.55	341.96
Materials out, grams		
Water	22.20	—
Diisobutylene	126.82	—
Isopropyl alcohol	—	150.10
Ester	190.00	189.21
Total	339.02	339.31
Loss, grams	3.53	2.65
Loss, %	1.03	0.78

[a] Operating conditions shown in Table V.
[b] Operating conditions shown in Table VI.

Table VIII. Comparison of Azeotropic Distillation and Transesterification Methods for the Preparation of Aliphatic Borate Esters

(Technical grade)

	Yield, %[a]		Ester Purity, %		
Borate Ester	Azeotropic distillation	Transesterification	Basis of calculation	Azeotropic distillation	Transesterification
Butyl	99.1	98.7	Boron	99.4	99.8
			Alcohol	97.2	99.4
Cyclohexyl	102.0	98.0	Boron	99.7	98.6
			Alcohol	97.6	97.8
2-Ethylhexyl	101.7	99.4	Boron	99.3	101.1
			Alcohol	97.3	100.0
2,6,8-Trimethyl-4-nonyl	99.8	100.1	Boron	99.0	98.4
			Alcohol	92.3	97.3
7-Ethyl-2-methyl-4-undecyl	101.3	101.2	Boron	99.4	101.2
			Alcohol	93.1	98.8

[a] Not adjusted for alcohol content.

It may be concluded that technical grades of borate esters having better than 90% purity (based on alcohol content) can be prepared in good yield (> 90%) by either azeotropic distillation or transesterification. Process flow diagrams illustrating both methods are shown for technical grade *n*-butyl borate (Figures 4 and 5).

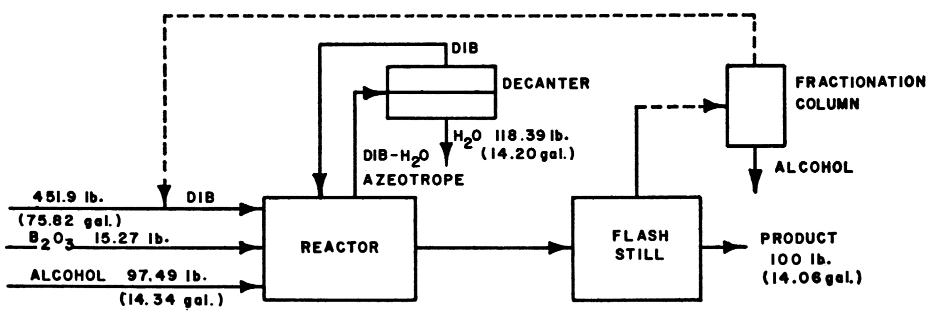


Figure 4. Flow diagram for batch preparation of *n*-butyl borate by azeotropic distillation

DIB. Diisobutylene

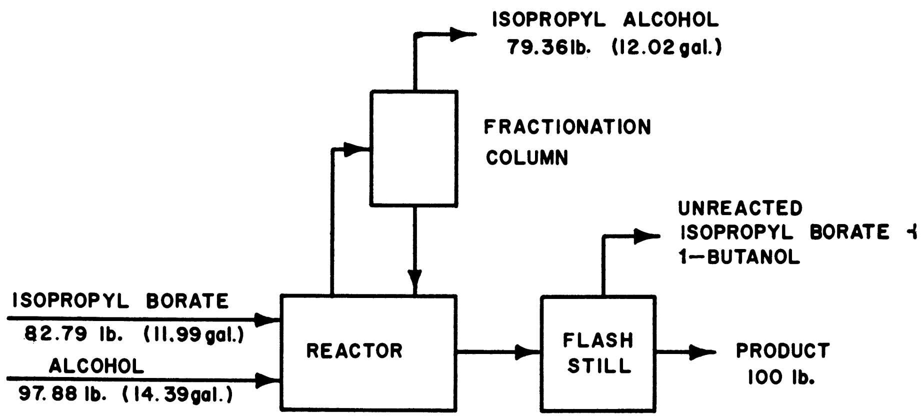
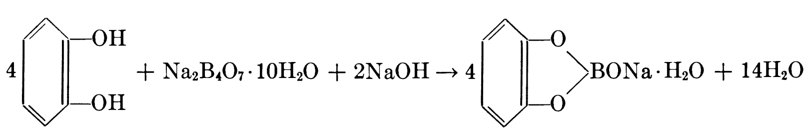


Figure 5. Flow diagram for batch preparation of *n*-butyl borate by transesterification

A similar process flow diagram for the previously reported continuous preparation of isopropyl borate (*120*) by Method III (dehydration with boron oxide) is given in Figure 6.

Borates of Polyhydric Compounds

Although catechol borate (IV), when prepared in an anhydrous medium, is hydrolyzed by water, its salts are stable (*65, 165–167*). The authors have synthesized sodium catechol borate monohydrate (formulated most simply as shown in Equation 10) by direct reaction of catechol (1.33 moles), borax (0.333 mole), and aqueous sodium hydroxide (0.665 mole):



(10)

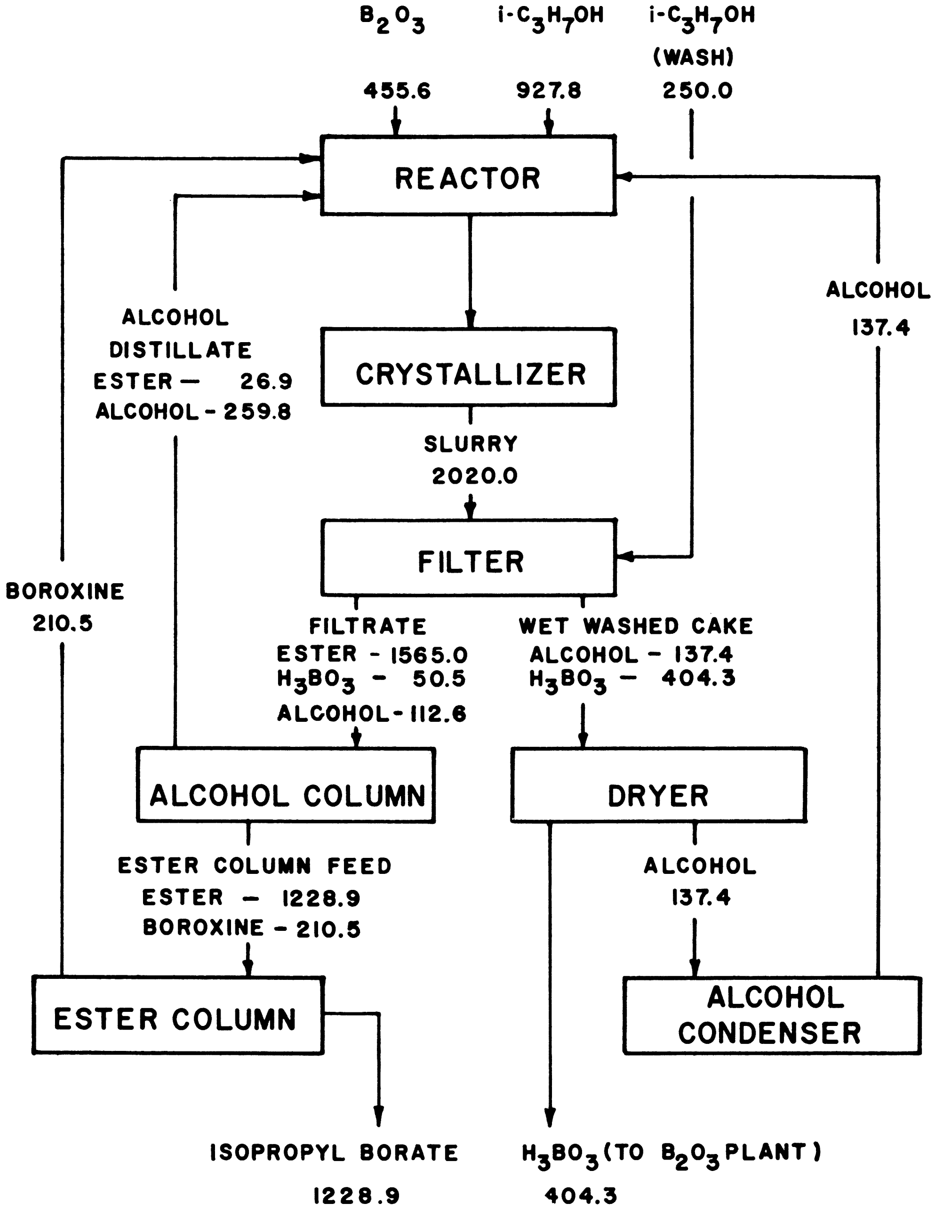


Figure 6. Flow diagram for continuous preparation of isopropyl borate by boric acid precipitation

After the reactants had been heated to 84°C., then cooled, the solids were removed by filtration and washed with ethyl alcohol to yield 217 grams (92.3%) of gray, shiny plates. Analysis of the vacuum-dried product gave:

Calculated for $C_6H_6O_4BNa$. Na, 13.08; B, 6.14
Found. Na, 12.97; B, 6.13

A number of viscous to glassy polymeric borates were briefly investigated to determine qualitatively the effect of cross linking on resistance to hydrolysis. As examples, boric acid, ethylene glycol, and phenol in a mole ratio of 1 to 2 to 0.3 gave a

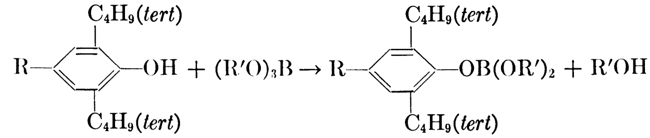
product which was viscous when hot and hard when cooled; a mole ratio of 1 to 2 to 1 yielded a material which was tacky at room temperature:

$$H_3BO_3 + HOCH_2CH_2OH + C_6H_5OH \xrightarrow[-H_2O]{} \left[-CH_2CH_2O-\underset{\substack{| \\ OC_6H_5}}{B}-O- \right]_n \qquad (11)$$

Reaction of boric acid and ethylene glycol alone resulted in a tacky product. These ethylene glycol borates were readily hydrolyzed by water. In contrast, the glassy copolymers obtained from the reaction of boric acid and maleic anhydride with glycerol and with pentaerythritol were only slowly attacked by water.

2,6-Di-*tert*-butylphenyl Borates

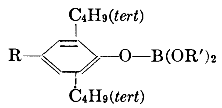
The authors have prepared a series of new, hydrolysis-resistant, mixed borate esters of 2,6-di-*tert*-butylphenols by the transesterification reaction (Method II):



(12)

These compounds, some physical constants for which are given in Table IX, are of considerable interest because of the high steric hindrance involved. The starting

Table IX. 2,6-Di-*tert*-butylphenyl-dialkyl Borates



Compound R	Compound R′	B.P., °C./Mm.	M.P., °C.
H—	Iso-C_3H_7—	80/0.5	—
CH_3—	Iso-C_3H_7—	—	88–89
CH_3—	n-C_4H_9—	140/0.6	—
CH_3—[a]	CH_2=CH—CH_2—	130–131/0.4	—
CH_3—[b]	$CH_3CH(\text{Iso-}C_3H_7)$—$CH_2CH(CH_3)_2$	153/0.5	—
(*tert*)C_4H_9—	Iso-C_3H_7—	—	209–215

[a] $d_4^{t°C.} = 0.9727 - 0.0007727\,t$.
$n_D^{t°C.} = 1.5004 - 0.0003794\,t$.
Viscosity (cs.) t°C. = $169^{6.6}$; $46.0^{23.2}$; $21.2^{37.8}$.

[b] $d_4^{t°C.} = 0.9121 - 0.0001700\,t$.
$n_D^{t°C.} = 1.4826 - 0.0003657\,t$.
Viscosity (cs.) t°C. = $521^{26.2}$; $208^{35.2}$; $85.5^{45.0}$.

phenols do not undergo the usual phenolic reaction—to form the sodium phenate, for example, it is necessary to use metallic sodium in liquid ammonia (*183*).

As an example of the hydrolysis resistance of the hindered esters, the 2,6-di-*tert*-butyl-4-methylphenyl diisopropyl borate was recovered quantitatively after 8 hours' reflux in 37.5% aqueous acetone followed by storage in the mother liquor for 13 weeks; no boron was found in the filtrate.

Details of the preparative methods for these compounds will be given in a subsequent publication.

Physical Properties

The physical properties of a number of borate esters have been summarized by Lappert (*116*) and by Steinberg and Hunter (*181*). Additional data have been obtained for several borates on the variation with temperature of vapor pressure (Tables X, XI), density (Table XII), refractive index (Table XIII), and viscosity

Table X. Vapor Pressures of Borate Esters

$\text{Log } p_{mm.} = A - B/T$

Borate Ester	A	B	B.P., °C. (Calcd.), 10 Mm.	References
Primary aliphatic				
Methyl[a]	8.1073	1785	68.3[760]	(181, 197)
Ethyl[b]	8.4156	2167	118[760]	(181, 197)
n-Butyl	8.3986	2804	106	(73, 181)
2-Ethylhexyl	9.4290	4080	211	(181)
n-Octyl	8.4776	3682	219	(181)
n-Decyl	9.4317	4478[c]	258	(116)
n-Dodecyl	8.2793	4126	294	(80, 181)
Secondary aliphatic				
Isopropyl	8.1877	2190	140[760]	(111, 181)
sec-Butyl	7.8840	2350	197[760]	(73, 181)
Methylisobutylcarbinyl	8.2400	2833	118	(164, 181)
2,6,8-Trimethyl-4-nonyl	8.4144	3585	210	(181)
2-Methyl-7-ethyl-4-undecyl	8.1154	3791	260	New compound
Aromatic				
o-Cresyl	9.0080	3883	212	(149, 181)
Miscellaneous				
2-Methoxyethyl	7.6396	2614	121	(164)
2-2′-Methoxyethoxyethyl	10.834	4457	180	New compound
Tri(hexyleneglycol) biborate	9.0910	3664	180	(123, 181)
Tetrahydrofurfuryl borate	12.576	5466	199	(76)

[a] Values from (197).

[b] Reference reported $\log p = 8.8553 - \frac{2298}{T}$.

[c] This value may be too low.

Table XI. Melting Points of Solid Borate Esters

Borate Ester	M.P., °C.[a]	References
Diisopropylcarbinyl	60.4–61.4	(164)
Diisobutylcarbinyl	97–98	(181)
Neopentyl glycol	123–124	(164)
Cyclohexyl	54–55	(198, 204)
Phenyl	89–91	(181, 204)
p-Cresyl[b]	137–140	(116)
2,5-Dimethylphenyl	147–148	New compound
3,4-Dimethylphenyl	72–73	New compound
3,5-Dimethylphenyl	145–148	New compound
2,6-Dimethylphenyl	156–157	New compound
2,6-Diisopropylphenyl	286–290	New compound

[a] Uncorrected.

[b] Sample probably impure.

Table XII. Densities of Borate Esters

$d_4^{t°C.} = A - Bt$

Borate Ester	A	B × 10⁴	d²⁰ (Calcd.)	References
Primary aliphatic				
Methyl	0.9578	13.62	0.9306	(181, 197)
Ethyl	0.8853	11.48	0.8623	(181, 197)
n-Propyl	0.8808	12.89	0.8550	(45, 181)
n-Butyl	0.8735	8.229	0.8570	(73, 181)
2-Ethylhexyl	0.8743	7.553	0.8592	(181)
n-Octyl	0.8661	6.658	0.8528	(181)
n-Decyl	0.8641	6.077	0.8519	(116)
n-Dodecyl	0.8704	7.654	0.8551	(80, 181)
Secondary aliphatic				
Isopropyl	0.8404	10.69	0.8190	(111, 181)
sec-Butyl	0.8495	9.043	0.8314	(73, 181)
Methylisobutylcarbinyl	0.8368	7.242	0.8223	(164, 181)
2,6,8-Trimethyl-4-nonyl	0.8544	7.393	0.8396	(181)
2-Methyl-7-ethyl-4-undecyl	0.8591	6.436	0.8462	New compound
Aromatic				
o-Cresyl	1.1037	7.515	1.0887	(149, 181)
m-Cresyl	1.0949	8.203	1.0784	(49)
2,4-Dimethylphenyl	1.0711	7.063	1.0570	New compound
Miscellaneous				
Allyl	0.9400	10.62	0.9188	(13, 93)
2-Methoxyethyl	1.0508	10.29	1.0302	(164)
2-2′-Methoxyethoxyethyl	1.0789	9.150	1.0606	New compound
Cyclohexyl	0.9992	8.330	0.9825	(198, 204)
3,3,5-Trimethylcyclohexyl	0.9249	7.184	0.9105	New compound
Tetrahydrofurfuryl	1.1214	7.360	1.1067	(76)

Table XIII. Refractive Indices of Borate Esters

$$n^{t°C.}_{D} = A - Bt$$

Borate Ester	A	B × 10⁴	n^{20} (Calcd.)	References
Primary aliphatic				
Methyl	1.3668	4.360	1.3581	(*181, 197*)
Ethyl	1.3825	4.359	1.3738	(*181, 197*)
n-Propyl	1.4029	4.000	1.3948	(*45, 181*)
n-Butyl	1.4129	2.949	1.4070	(*73, 181*)
2-Ethylhexyl	1.4441	3.615	1.4369	(*181*)
n-Octyl	1.4430	3.496	1.4360	(*181*)
n-Decyl	1.4492	3.487	1.4422	(*116*)
n-Dodecyl	1.4546	3.484	1.4476	(*80, 181*)
Secondary aliphatic				
Isopropyl	1.3850	4.380	1.3762	(*111, 181*)
sec-Butyl	1.4038	4.026	1.3957	(*73, 181*)
Methylisobutylcarbinyl	1.4182	3.895	1.4104	(*164, 181*)
2,6,8-Trimethyl-4-nonyl	1.4453	3.513	1.4383	(*181*)
2-Methyl-7-ethyl-4-undecyl	1.4543	3.333	1.4476	New compound
Aromatic				
o-Cresyl	1.5637	3.718	1.5563	(*149, 181*)
m-Cresyl	1.5637	4.077	1.5555	(*49*)
2,4-Dimethylphenyl	1.5535	3.282	1.5469	New compound
Miscellaneous				
Allyl	1.4359	4.471	1.4270	(*13, 93*)
2-Methoxyethyl	1.4235	3.743	1.4160	(*164*)
2-2′-Methoxyethoxyethyl	1.4418	3.385	1.4350	New compound
3,3,5-Trimethylcyclohexyl	1.4658	3.487	1.4588	New compound
Tri(hexyleneglycol) biborate	1.4457	3.362	1.4390	(*123, 181*)
Tetrahydrofurfuryl	1.4674	3.308	1.4608	(*76*)

Table XIV. Viscosities of Borate Esters

Borate Ester	Temp., °C.	Viscosity, Centistokes	Temp., °C.	Viscosity, Centistokes	Temp., °C.	Viscosity, Centistokes
Primary aliphatic						
Methyl	21.2	0.416	39.8	0.347	60.0	0.295
Ethyl	21.4	0.615	40.0	0.503	60.0	0.424
n-Propyl	7.0	1.59	23.8	1.09	43.4	0.845
n-Butyl	21.4	1.99	39.8	1.47	63.6	1.08
2-Ethylhexyl[a]	20.8	11.0	39.6	6.18	60.0	3.80
n-Octyl	20.6	11.1	40.0	6.38	60.0	3.93
n-Decyl	21.4	19.3	40.0	10.3	60.0	6.66
n-Dodecyl	21.0	30.5	39.6	15.1	60.0	8.89
Secondary aliphatic						
Isopropyl	21.4	1.03	39.6	0.797	59.8	0.631
sec-Butyl	20.8	1.90	39.6	1.37	60.0	1.04
Methylisobutylcarbinyl	21.4	4.30	40.0	2.77	63.6	1.70
2,6,8-Trimethyl-4-nonyl	21.4	121.	39.6	33.7	60.0	15.4
2-Methyl-7-ethyl-4-undecyl	20.6	139.	39.6	46.5	63.6	16.9
Aromatic						
o-Cresyl	21.4	175.	39.8	35.9	60.0	11.9
m-Cresyl	20.6	192.	39.6	37.0	60.0	10.8
2,4-Dimethylphenyl	60.0	35.1	70.0	17.3	76.6	12.8
Miscellaneous						
Allyl	7.0	1.25	23.2	0.902	37.8	0.747
2-Methoxyethyl	21.2	2.90	39.8	1.99	59.8	1.39
2-2′-Methoxyethoxyethyl	20.8	8.57	39.6	5.05	60.2	3.23
3,3,5-Trimethylcyclohexyl	60.0	87.9	70.0	43.3	79.0	25.5
Tri(hexyleneglycol) biborate	23.4	433.	37.8	97.8	48.2	44.5
Tetrahydrofurfuryl	21.4	22.6	40.0	6.93	60.0	4.35

[a] (*100*) report 1.94 (210°F.); 6.28 (100°F.); 433 (−40°F.).

(Table XIV). These data were fitted by the method of least squares. The melting points of some solid esters are given in Table XI.

The vapor pressure data were obtained with the modified Cottrell ebullioscope shown in Figure 7 (designed by H. S. Myers, C. F. Braun Co., Alhambra, Calif.; constructed by Stanford Glassblowing Laboratories, Palo Alto, Calif.) using a Cartesian manostat (Emil Greiner Co., New York, N. Y.) to maintain reduced pressures. Densities were determined in 5- and 10-ml. volumetric flasks with extended necks, calibrated with distilled water, and suspended in a constant temperature bath. The refractive indices were determined with an Abbé refractometer (Bausch & Lomb

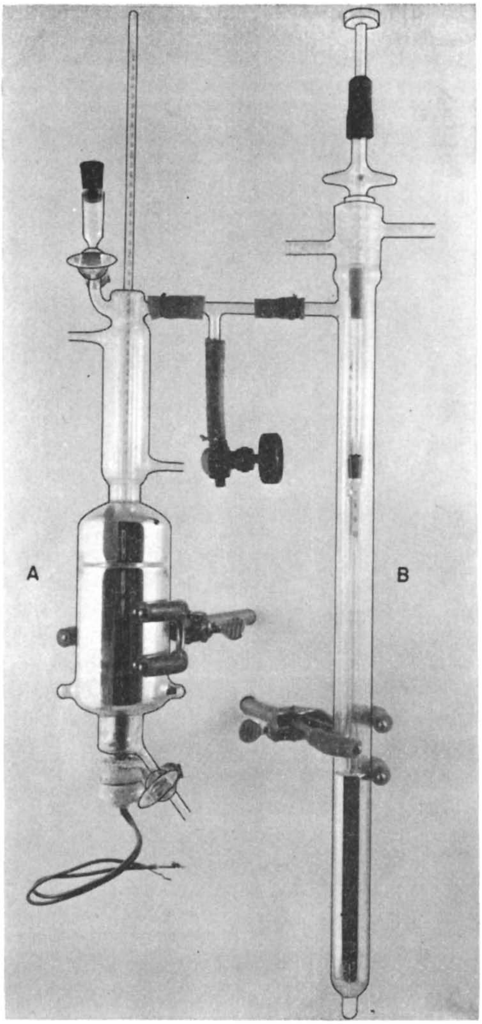


Figure 7. Modified Cottrell ebullioscope of H. S. Myers

A. Ebullioscope
B. Cartesian manostat

Optical Co., Type 33–45–56), calibrated with distilled water, having water at the required temperature circulating through the prism. Viscosities were determined in Cannon-Fenske-Ostwald viscometers (Cannon Instrument Co., State College, Pa.) suspended in a constant temperature bath.

Average densities of primary aliphatic, secondary aliphatic, and aromatic borates are given in Figure 8. The relatively high density of methyl borate may be attributed to shortening of the B—O bond length, as shown by a shift of the infrared B—O stretching vibration from the average of 1335 cm.$^{-1}$ for alkyl borates to 1352 cm.$^{-1}$

The refractive indices of primary and secondary aliphatic borates are shown in Figure 9 as a function of the number of carbon atoms in the alcohol moiety.

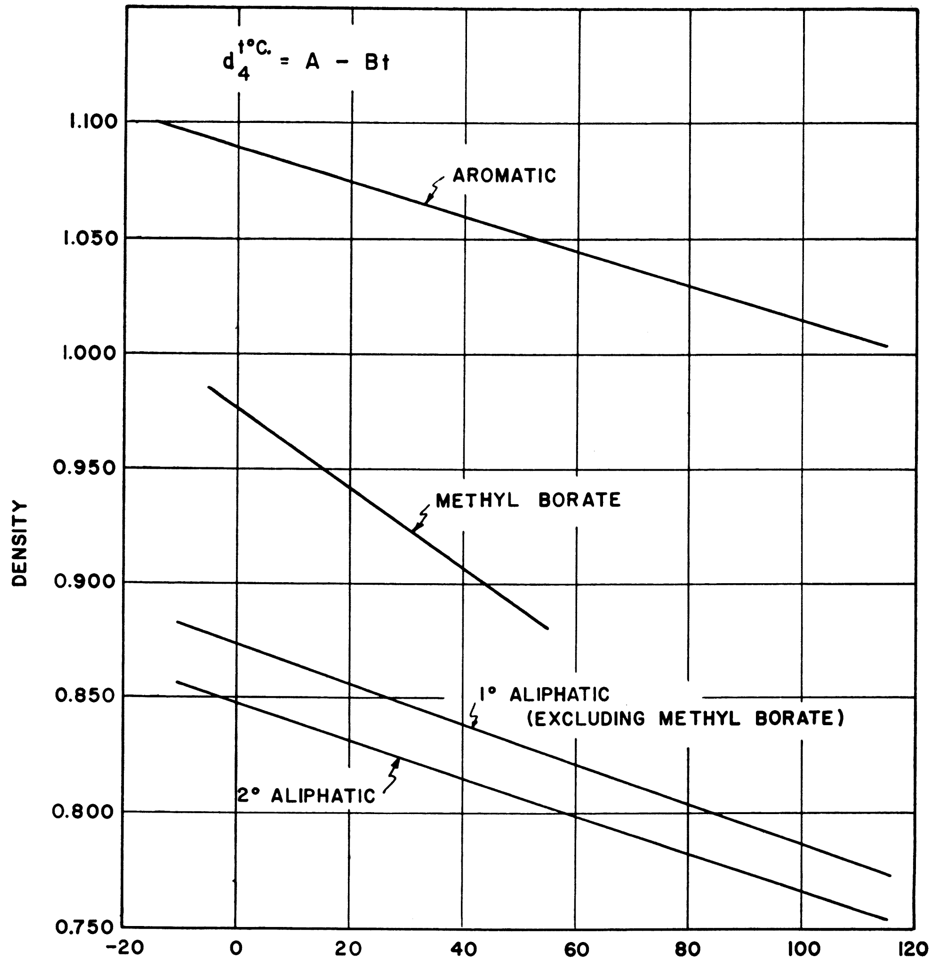


Figure 8. Densities of borate esters

Investigation of the specific viscosity of dilute solutions of long-chain borate esters (*n*-octyl to *n*-decyl) in benzene and carbon tetrachloride indicated that the esters are in extended form as expected from the parachor values (*7*).

The planar configuration of the BO_3 group was demonstrated by an electron diffraction study of methyl borate (*16*). The bond angles were found to be 120° for B—O, and 113° ± 3° for B—O—C. The bond distances were: B—O, 1.38 ± 0.02 A.; C—O, 1.43 ± 0.03 A. The data suggested considerable rotation of the CH_3 groups about the line of the B—O bond; this internal rotation was interpreted as being synchronized so that the C—C distance is always greater than 3.5 A., as there appeared to be insufficient room for independent movement. To this synchronization of the methyl groups was attributed a small dipole moment.

The parachor constants for boron in simple alkyl borates were found to range from 15.9 to 17.8 (*185*). Subsequently, Jones and others (*93*) found that tri-2-chloroethyl borate, $B(OCH_2CH_2Cl)_3$, and tri-2,2-dichloroisopropyl borate,

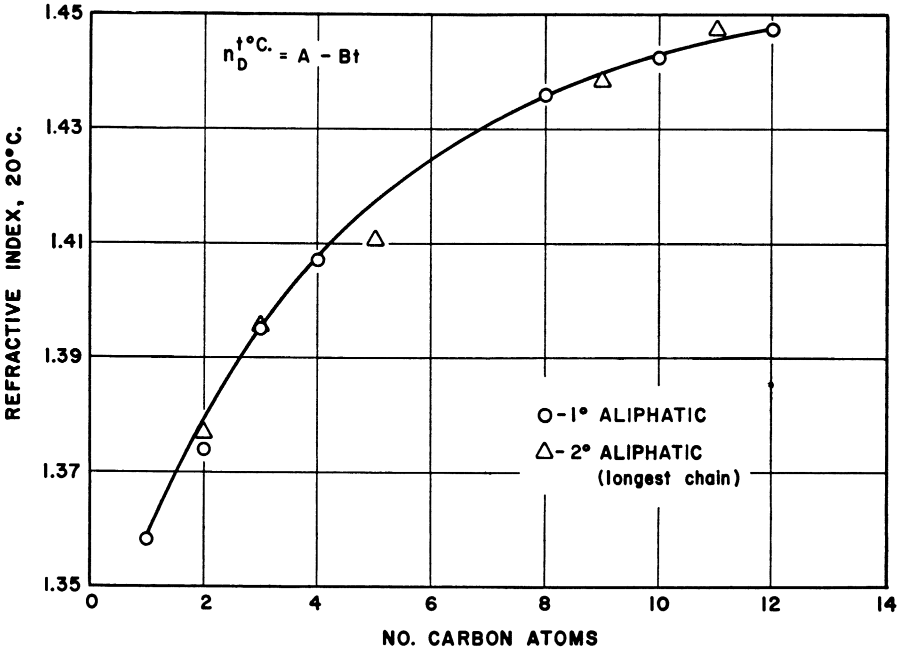


Figure 9. Refractive indices of borate esters

$B[OCH(CH_2Cl)_2]_3$, have boron parachor constants of 21.6 and 37.1, respectively. They concluded that the value of the constant rises with increasing molecular weight and complexity of the boron compound.

Arbuzov and Vinogradova (*8*) also measured the parachor for the following borates: methyl (243.7); ethyl (363.1); *n*-propyl (476.5); isopropyl (475.8); *n*-butyl (597.9); *n*-heptyl (957.7); *n*-octyl (1072.2); and *n*-decyl (1307.2). They assigned the value 77.5 to the $B(O—C)_3$-group. These parachor data were said to be in agreement with the electron diffraction measurements of Bauer and Beach (*16*) and to confirm the planar structure of the BO_3 group, with out-of-plane synchronous movement of the alkyl groups so that if one is above the BO_3-group plane, two are below the plane.

Chemical Properties

Thermal Stability. Brandenberg and Galat (*30*) described the pyrolysis of alcohols to form olefins in 85 to 95% yields at 350°C. using boric acid as a catalyst. The reaction was said to proceed by formation and subsequent decomposition of the corresponding alkyl borate; the position of the olefin double bond was not indicated. The unstable intermediate may, however, be the metaborate formed from the initial borate ester (*142*). Dreisbach, Martin, and Erbel (*55*) stated that borates of α-hydroxyalkyl aromatic compounds were thermally decomposed when they were distilled at 10 mm., but did not describe the decomposition products. Pyrolysis of dodecyl borate gave the α-olefin (*9*).

The authors investigated the thermal stability of borate esters at atmospheric pressure by heating approximately 50 ml. of the selected compound under reflux for 1 hour in a 100-ml. flask sealed to a jacketed Vigreux column. After the reflux period, approximately 50% by volume of the ester was distilled at atmospheric pressure. Both distilland and distillate were analyzed for boron as a measure of

the amount of decomposition that had occurred. The decomposition products were not examined.

Methyl, ethyl, and isopropyl borates are stable at their atmospheric boiling points (*197*). The results of the study given in Table XV show that the higher esters

Table XV. Stability of Borate Esters to Distillation at Atmospheric Pressure[a]

Borate Ester	% B Theoretical	Distillate	Distilland
n-Butyl	4.70	4.63	4.72
2-Ethylhexyl	2.71	2.65	2.84
Cyclohexyl	3.51	3.30	3.85
2-Methyl-4-pentyl	3.44	3.37	3.43
2-Methyl-7-ethyl-4-undecyl	1.66	0.39	2.96
n-Dodecyl	1.91	0.87	4.29
(*m*,*p*)-Cresyl	3.26	1.99	3.43
Tetrahydrofurfuryl	3.44	1.18	4.52

[a] Preceded by 1-hour reflux.

undergo thermal decomposition, as evidenced by the decreasing boron content of the distillate while that of the distilland increases. All these esters may be successfully distilled under reduced pressure, although the temperature should probably be kept below about 250°C. to prevent decomposition.

Reactions. Scattergood, Miller, and Gammon (*164*) observed qualitatively that branching reduces the rate of hydrolysis of alkyl borates. Quantitative data were obtained by Steinberg and Hunter (*181*), who observed the time of disappearance of the phenolphthalein end point when half the caustic required for complete hydrolysis was added to the ester in aqueous dioxane. They found that the relative rates for aliphatic and alicyclic esters are in the order expected from the steric factors involved in the nucleophilic attack of water (or hydroxyl ion) on the central boron atom (see Discussion). The rate of hydrolysis is, therefore, reduced by increasing size of the alcohol group and by branching so that, for example, butyl > amyl > hexyl, etc., and primary > secondary > tertiary. The rapid hydrolysis of highly hindered aromatic and chlorine-substituted aliphatic esters was attributed to a shift from steric to electronic controlling factors.

Bradley and Chrisopher (*29*) investigated the hydrolysis of alkyl borates in anhydrous acetone. They reported the equilibrium constants at 0°C. to be methyl borate, 16.0; *n*-propyl borate, 2.7; *n*-butyl borate, 2.1; and *n*-amyl borate, 1.8.

Borate esters react with carboxylic acids to form the corresponding esters (*85, 86, 170*):

$$(RO)_3B + 3R'COOH \rightarrow 3R'COOR + H_3BO_3 \qquad (13)$$

The reaction with acetic anhydride to form boron acetate has also been described (*120*):

$$2(RO)_3B + 5(CH_3CO)_2O \rightarrow (CH_3COO)_2BOB(OOCOH_3)_2 + 6CH_3COOR \qquad (14)$$

Friedel-Crafts alkylations have been carried out with borate esters in place of the alkyl or alkaryl halide. For example, with aluminum chloride as catalyst, isobutyl borate reacted with *m*-xylene to form *tert*-butylxylene, with anisole to form *p*-*tert*-butylanisole, with phenol to form *p*-*tert*-butylphenol, and with bromobenzene to form *p*-bromo-*tert*-butylbenzene; benzyl borate and benzene gave diphenylmethane (*96*). Benzene and butyl borate, with aluminum chloride, gave an unidentified organoboron compound, leading to the conclusion that the borate esters may either donate the alkyl group or add boron to the benzene ring (*191*).

Aluminum isopropoxide has been used to reduce aldehydes and ketones in the Meerwein-Pondorff-Verley reaction (*203*). Somewhat lower yields at higher tempera-

tures (150° to 175°C.) were obtained by Kuivila, Slack, and Siiteri (*111*), who investigated the use of alkyl borates for the same purpose:

$$\left(\begin{matrix}R \\ \quad \diagdown \\ \quad\quad CHO \\ \quad \diagup \\ R\end{matrix}\right)_3 B + 3R'COR'' \rightarrow 3RCOR + \left(\begin{matrix}R' \\ \quad \diagdown \\ \quad\quad CHO \\ \quad \diagup \\ R''\end{matrix}\right)_3 B \qquad (15)$$

Aromatic aldehydes were reduced in good yield by isopropyl borate; aliphatic aldehydes gave poor yields. Ketones were not reduced by isopropyl borate and only in low yield by allyl borate.

The borate esters react with Grignard reagents to give, successively, boronic acids, $RB(OH)_2$; borinic acids, R_2BOH; and borines, R_3B (*98*). The mechanism of this reaction has been discussed in some detail (*196*).

Of the alkyl borates, only methyl borate appears to react with ammonia and primary and secondary amines to form stable, solid coordination compounds (*77–79, 168, 193*):

$$(CH_3O)_3B + R_xNH_{3-x} \rightarrow (CH_3O)_3B \cdot NH_{3-x}R_x \qquad (16)$$

The aryl borates, which are stronger Lewis acids than the alkyl esters, generally form similar compounds, with some steric limitations (*47, 48*).

A number of borate esters were investigated as catalysts for the polymerization of diazomethane to polymethylene (*131*). The order of effectiveness was approximately in the order of increasing acidity of the esters: isopropyl < ethyl < methyl <allyl < benzyl < β-methoxyethyl < β-chloroethyl < β-trichloroethyl.

Borate esters react with metal alkoxides to form the corresponding metal tetraalkoxyborohydride (*171*):

$$(RO)_3B + NaOR \rightarrow NaB(OR)_4 \qquad (17)$$

However, steric limitations appear to decrease the rate of formation and stability of the tetraisopropoxy compound. Reaction with metal hydrides yields the corresponding metal trialkoxyborohydrides:

$$(RO)_3B + NaH \rightarrow NaBH(OR)_3 \qquad (18)$$

Tetracoordinate Boron in Borates

The ability of boron compounds to act as Lewis acids has long been known and the effect has been used to correlate various aspects of boron chemistry. For example, Schlesinger and Brown (*171*) used the Lewis generalized acid-base concept to correlate the reactions of diborane and related compounds. Brown (*34*) has given an excellent summary of his work (concerned to a great extent with the coordination of various bases with boron compounds) on the chemical effects of steric strains.

Kuivila and coworkers (*105–114*) have determined kinetically that a tetracoordinate boronate anion is the important intermediate in the electrophilic displacement of the boronate moiety from areneboronic acids by halogen or peroxide.

Böeseken and coworkers (*24*) confirmed the tetracoordinate structure of the boron atom in *cis*-diol compounds by separating the optical isomers of boron bis-(γ-chlorocatechol) and boron bis-(3-nitrocatechol).

The importance of tetracoordinate boron during the preparation of benzeneboronic acid from methyl borate and phenylmagnesium bromide has been demonstrated (*196*).

Although there are many examples of tetracoordinate boron compounds, comparatively little is known about the factors affecting the Lewis acidity of borate esters. Evidence is available to support the hypothesis that boron compounds undergo reaction by coordination with a base. For example, when an optically active borate is hydrolyzed, the alcohol formed retains its configuration (*72, 164*), indicating cleavage

of a boron-oxygen bond. This could occur as shown in Figure 10. The second and third steps of the hydrolysis are identical to the first. The fourth step probably leads to the tetrahydroxyborate anion (*61*). Whether the hydrolysis is concerted or

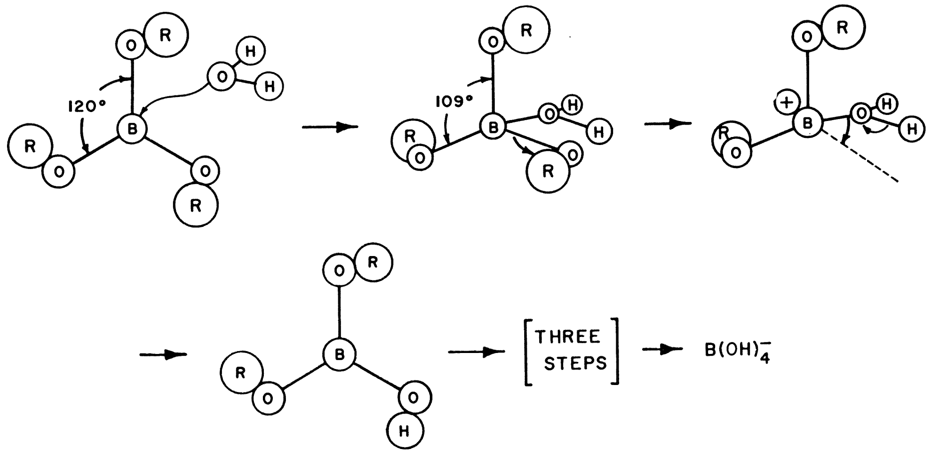


Figure 10. Hydrolysis and reaction mechanism involving tetracoordinate boron

stepwise is not definitely known, but a stepwise mechanism is suggested, or perhaps a "stepwise-concerted" mechanism, in which solvent is first displaced by another base (water for hydrolysis) as shown in Figure 11, followed by the mechanism depicted in Figure 10.

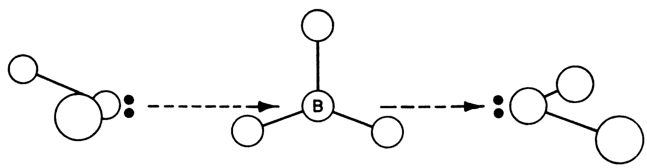


Figure 11. Generalized displacement mechanism applied to borate esters

Such a mechanism would explain why the rates of hydrolysis of borate esters are much slower in aqueous acetone, tetrahydrofuran, and dioxane or other Lewis bases with an unhindered electron pair than in aqueous methanol. Further evidence supporting this mechanism for hydrolysis (and reaction) is afforded by comparing the relative inertness of tertiary amine–boron trichloride coordination compounds to cold water with the almost violent hydrolysis of boron trichloride itself. This is also true for sodium tetramethoxyborohydride and trimethyl borate; the borohydride is only slowly hydrolyzed, whereas the borate ester hydrolyzes very rapidly.

The authors have investigated the infrared spectra of borate esters. Bethell and Sheppard (*21*) reported a very strong absorption at 1450 cm.$^{-1}$ for crystalline boric acid. This was assigned to a symmetrical B—O stretching, as it did not change appreciably for deuterated boric acid. Werner and O'Brien (*198*) determined the infrared spectra of several borate esters. They assigned the strong band at 1340 ± 10 cm.$^{-1}$ to the B—O stretching vibration. The authors find an average of 1335 cm.$^{-1}$ for B—O stretching in alkyl borate esters (Table XVI) and an average of 1354 cm.$^{-1}$ for aryl borate esters. Absorption bands for the stable, mixed alkyl-aryl borates are shown in Table XVII.

Table XVI. Infrared Data for Aliphatic Borate Esters

Borate Ester	$Cm.^{-1}$
Methyl	1352 VS 683 W 662 M
Ethyl	1335 VS 693 W 665 M
n-Propyl	1334 VS 692 W 667 M
n-Butyl	1335 VS 690 W 663 M
n-Octyl	1336 VS 690 W 664 M
2-Ethylhexyl	1334 VS 688 W 663 M
n-Decyl	1337 VS 690 W 664 M
n-Dodecyl	1337 VS 688 W 663 M
Isopropyl	1327 VS 692 W 663 M
sec-Butyl	1332 VS 688 VW 663 M
Cyclohexyl	1325 VS 688 W 662 M
Methylisobutylcarbinyl	1330 VS 687 W 663 M
Diisopropylcarbinyl	1334 VS 678 W 657 M
Diisobutylcarbinyl	1340 VS 681 W 661 M
3,3,5-Trimethylcyclohexyl	1338 VS 690 VW 664 M
3,6,8-Trimethylnonyl	1335 VS 681 W 657 M
Tetradecyl	1330 VS 680 W 657 M
2-Methoxyethyl	1333 VS 686 W 662 M
2-2′-Methoxyethoxyethyl	1333 VS 684 W 661 M
Tetrahydrofurfuryl	1334 VS 686 W 662 M
Tri(hexyleneglycol) biborate	1309 VS 690 W 664 M

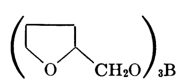
Table XVII. B—O Absorption for Aromatic and Mixed Aliphatic-Aromatic Esters

Borate Ester	Cm.$^{-1}$	Phase
Aromatic Esters		
Phenyl	1354	CCl_4
o-Cresyl	1357	Film
n-Cresyl	1352	Film
p-Cresyl	1354	CCl_4
		Film
3,5-Dimethylphenyl	1356	CCl_4
	1356	C_6H_{12}
3,4-Dimethylphenyl	1352	CCl_4
2,4-Dimethylphenyl	1352	Film
2,6-Dimethylphenyl	1358	$CHCl_3$
2,6-Diallylphenyl	1353	$CHCl_3$
2,6-Diisopropylphenyl	1353	CCl_4
6-Chloro-1-cresyl	1353	CCl_4
Mixed Aliphatic-Aromatic Esters		
2,6-Di-*tert*-butyl-4-methylphenyldiallyl	1329	Film
2,6-Di-*tert*-butyl-4-methylphenyldiisopropyl	1319	KBr
	1328	
2,6-Di-*tert*-butyl-4-methylphenyldi-*n*-butyl	1333	CCl_4
	1335	$CHCl_3$
	1325	Film

In addition two bands seem to be very characteristic of aliphatic borates (Figure 12). Werner and O'Brien (*198*) observed a weak band for aliphatic borate esters at about 690 cm.$^{-1}$ but did not state whether or not they considered it to be characteristic. Their instrument did not permit observation of the second, medium band at 662 ± 5 cm.$^{-1}$ The shorter wave length band has been found at 687 ± 8 cm.$^{-1}$ (Table XVI). Although no definite assignment has been made, the fact that the two bands are nearly constant regardless of a considerable mass change in going from methyl through tetradecyl groups suggests assignment to movement of the boron atom above and below the plane of the oxygen atoms (ν_2 for D_3h symmetry).

The authors have also observed two consistent bands which are believed to be due to tetracoordinate B—O: a weak to very weak band at 1250 cm.$^{-1}$, and a weak to medium band at 1178 to 1200 cm.$^{-1}$ (Table XVIII). To calculate (*75*) the tetra-

Table XVIII. Materials Showing Absorption at 1250 and 1178 to 1200 Cm.$^{-1}$

Material	Cm.$^{-1}$
$(CH_3O)_3B$	1250 W 1178 M
$(CH_3O)_3B \cdot CH_3OH$	1250 W 1179 M
$(CH_3O)_3B \cdot n\text{-}C_4H_9OH$	1262 M 1180 M
$(n\text{-}C_4H_9O)_3B \cdot CH_3OH$	1259 W 1193 VW
$NaBH(OCH_3)_3$	1253 W 1184 M
$NaB(OCH_3)_4$	1262 W 1194 S
$(C_2H_5O)_3B$	— 1190 W
$(CH_2{=}CHCH_2O)_3B$	— 1200 VW
$(n\text{-}C_3H_7O)_3B$	— 1197 VW
$(n\text{-}C_4H_9O)_3B$	— 1195 VW
$(CH_3OCH_2CH_2O)_3B$	— 1200 S
$(CH_3OCH_2CH_2OCH_2CH_2O)_3B$	— 1198 S
	— 1186 S
Tri(hexyleneglycol) biborate	— 1177 S

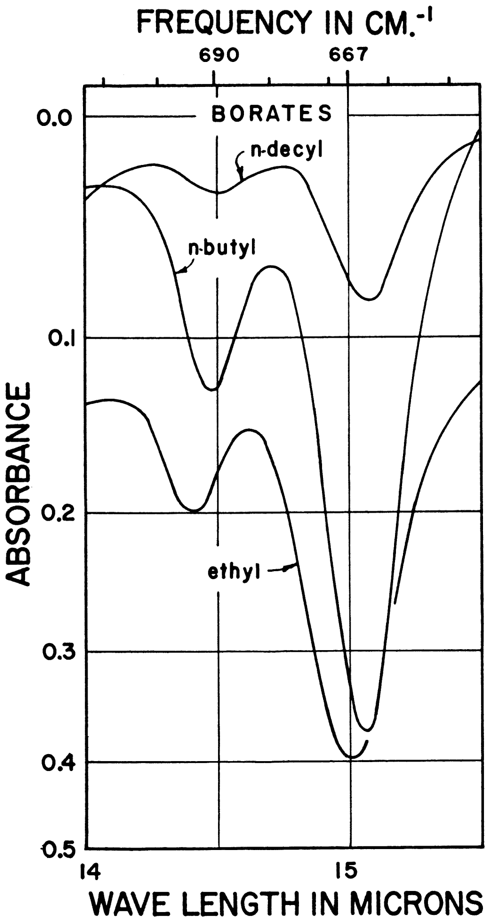
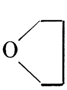


Figure 12. Infrared absorption of aliphatic borate esters in the region from 650 to 700 cm.$^{-1}$

coordinate B—O absorption required that the bond distance be found in order to estimate the force constant. It was first assumed that the percentage increase in bond length for B—O trigonal coplanar going to B—O tetracoordinate would be the same as for B—F. This led to an estimated tetracoordinate B—O length of 1.46 A., which corresponds closely to the reported (*17*) B—O bond distance of 1.50 ± 0.06 A. for dimethyl ether–boron trifluoride and to the sum of the single bond radii, 1.54 A. (*145*). Using a bond distance of 1.50 A., the calculated absorption for tetracoordinate B—O would be 1211 cm.$^{-1}$ The intensities of the two bands found vary directly with the basicity of the solvent. For example, mixtures of methyl borate with ethers (Figure 13) have intensities in the order:

$(CH_3O)_3B:O$  $> (CH_3O)_3B:O(C_2H_5)_2 \gg (CH_3O)_3B\cdot O(C_4H_9)_2$

The bands at 1250 and especially at 1190 cm.$^{-1}$ are similarly more intense in the tetra-

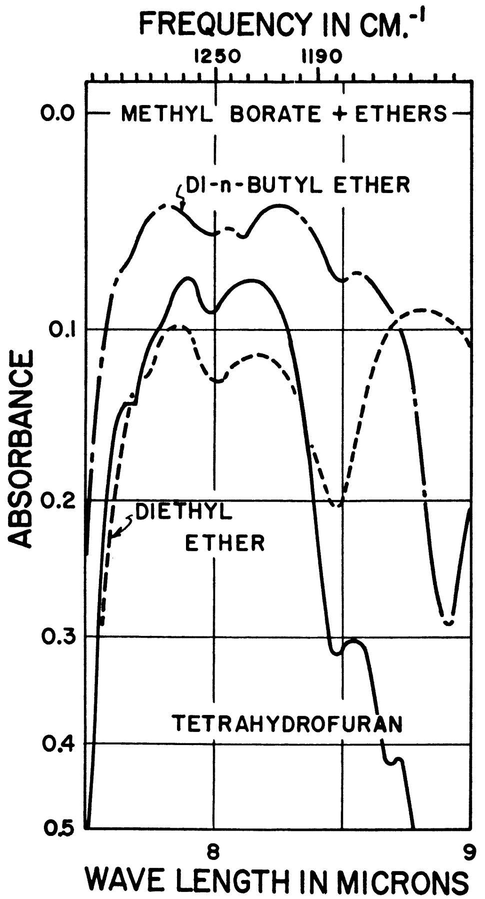
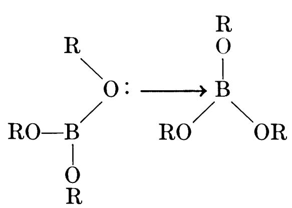


Figure 13. Infrared absorption of methyl borate with ethers in the region from 1110 to 1300 cm.$^{-1}$

coordinate boron compounds, sodium tri- and tetramethoxyborohydride (Figure 14).

A study of this spectral region also indicates weak interaction of oxygen in one methyl borate molecule with boron in another molecule (Table XVIII):



This is also observed for methanol–methyl borate (Figure 14), confirming the formulation of Syrkin and Dyatkina (*186*). It is significant that with increasing steric interference of the Lewis acid (borate) and base (ether), the absorptions at 1250 and

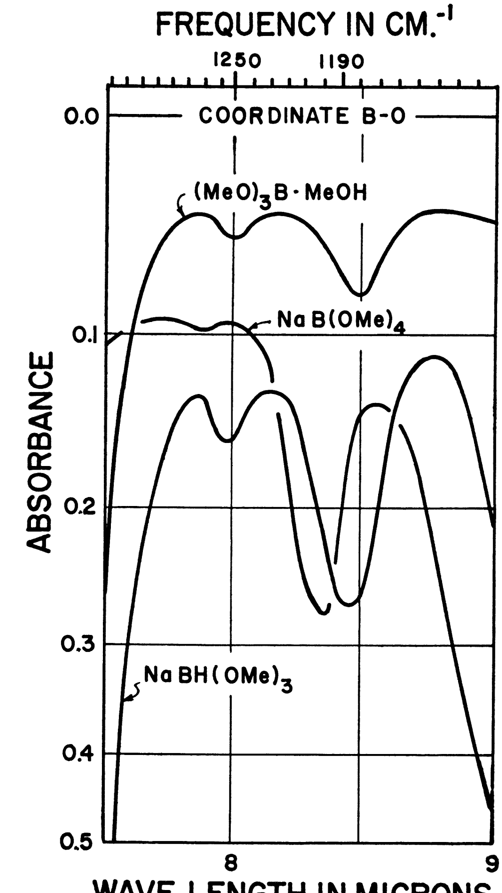


Figure 14. Infrared absorption of tetracoordinate boron compounds in the region from 1110 to 1300 cm.$^{-1}$

1190 cm.$^{-1}$ disappear, the absorption at 1250 cm.$^{-1}$ disappearing first. The intensities of the absorptions for the esters are in the order (Table XVIII):

$$(CH_3O)_3B > (C_2H_5O)_3B > (CH_2{=}CHCHO)_3B > (n\text{-}C_3H_7O)_3B > (n\text{-}C_4H_9O)_3B$$

This ester absorption was not seen for other aliphatic borate esters unless they also contained ether oxygen; the esters 2-methoxyethyl, 2-[2′-methoxyethoxy]ethyl, tetrahydrofurfuryl borate, and tri(hexyleneglycol) biborate all show medium to strong absorptions, further suggesting oxygen-boron intramolecular interaction.

The spectra of the aryl borates are more complex and no correlations have yet been made. It appears that there is an absorption maximum just outside the range of rock salt optics (650 cm.$^{-1}$) for all of the aryl borates. Further details will be presented in a subsequent paper.

Toxicity

Little information appears to have been published about the toxicity of borate esters. In screening tests with ethyl and butyl borates the following were found (*41*):

Test	Triethyl Borate	Tributyl Borate
Snail control	Mortality 1/10 at 10 p.p.m.	Mortality 0/10 at 10 p.p.m.
Toxicity	Mouse mortality 0/3 at 15.6 cu. mm./kg.; ataxia at 125 to 500 cu. mm./kg. No response in brown trout, bluegill, goldfish	Mouse mortality 1/5 at 500 cu. mm./kg.; ataxia, depression; recovery in 20 min.
Antibacterial	Slight activity against *S. aureus;* negative against *B. globigii*	Negative against *S. aureus, E. coli, B. globigii*
Plant growth regulator	No apparent effect on red kidney bean seeds	—
Cancer	—	Negative results at 225 cu. mm./kg.

Sax (*163*) cites experimentally induced eye damage from methyl and ethyl borates. In general, for esters which hydrolyze rapidly, it seems reasonable to ascribe the principal effects to the resulting alcohol or (phenol) and boric acid. Boric acid is said to

Table XIX. Uses of Borate Esters

Use	References
Antidiscolorant (aromatic amines)	(*176*)
Antioxidant	
Alcohol	(*83*)
Rubber	(*38, 144*)
Azeotropic separation	(*184*)
Catalyst	
Cracking	(*199*)
Oxidation acetylenic γ-glycols	(*33*)
Polymerization diazomethane	(*131*)
Polymerization drying oils	(*201*)
Sulfurization fatty oils	(*63*)
Synthesis β-lactones	(*81*)
Coating	
Flame-resistant	(*12*)
Water-repellant	(*143*)
Colorimetric reagent (hydroxyquinones)	(*5*)
Cosmetic preparations	(*10, 19, 76*)
Curing agent (epoxy resins)	(*62*)
Dehydrating agent	
Hydrogen peroxide	(*121*)
Polymerization silicones	(*153*)
Road aggregates	(*132, 177, 178*)
Deterrent (smokeless powder)	(*162*)
Electrolytic condensers	(*10, 19, 31, 60, 68–71, 148, 160*)
Flux (brazing, welding)	(*6, 126, 168, 196*)
Fungicide	(*149, 187*)
Gelling agent (castor oil)	(*66, 135*)
Germicide	(*90, 149*)
Inhibitor (SO_3 polymerization)	(*127*)
Insecticide	(*1, 55*)
Lubricant (textile)	(*200*)
Petroleum additive	
Antioxidant	(*44, 54, 49, 117, 154*)
Corrosion inhibitor	(*44, 54, 174, 190*)
Dehydrating agent	(*64*)
Demulsifier	(*99*)
Improve gasoline performance	(*52, 67, 88, 117*)
Prevent wax precipitation	(*122*)
Pharmaceutical preparations	(*10, 11, 19, 31, 42, 43, 50, 51, 125, 152, 189*
Plasticizer	(*18, 31, 80, 103, 138, 162, 173*)
Polymer	
Adhesive	(*10, 19, 31, 138, 150*)
Binder	(*46, 138*)
Coating	(*10, 19, 31*)
Resin	(*10, 13, 19, 22, 28, 31, 32, 46, 57, 82, 89, 104, 128, 139, 156, 157, 175*)
Purification	
Alcohols, phenols	(*37, 40, 84, 97, 101, 123, 133, 141, 158, 205*)
Cottonseed oil	(*169*)
Recovery boron values (saltpeter)	(*39*)
Refractories (bonding, impregnation)	(*194*)
Resin modifier (pine wood resin)	(*161*)
Rubber accelerator	(*65*)
Stabilizer (PVA films)	(*22, 115*)
Surface active agent (detergent, dispersant, emulsifier, foaming, wetting)	(*20, 31, 74, 80, 91, 94, 95, 124, 129, 130, 140, 147, 159, 162, 192*)
Wax or resin substitute	(*182*)

affect the central nervous system and to accumulate in the brain, liver, and body fat. Sax states that the fatal dose of orally ingested boric acid is 15 to 20 grams for adults and 5 to 6 grams for infants. Spector (*179*) gives the boric acid range of LD_{50} for laboratory animals as 4740 to 5580 mg. per kg.

For 2,6-di-*tert*-butyl-4-methylphenyl diisopropyl borate, one of the new stable esters shown in Table IX, the oral LD_{50} in rats was found to be 5.2 grams per kg. (toxicity test conducted by Scientific Associates, St. Louis, Mo.), which is in good agreement with the value just cited for boric acid.

Uses of Borate Esters

In addition to the synthetic possibilities for borate esters, a large number of miscellaneous uses have been described, principally in the patent literature. Some of these are summarized in Table XIX.

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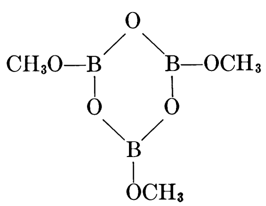
Trimethoxyboroxine—An Extinguishing Agent for Metal Fires

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Metal fires present a serious problem to the producers and processers of such metals as magnesium, titanium, and zirconium. Titanium and zirconium in the form of sponge, and all of these metals in the form of chips or turnings, will ignite easily and, when burning, their combustion will be supported even by nitrogen. Trimethoxyboroxine, an organic ester of boric oxide, is a liquid having unique characteristics which are useful for extinguishing such metal fires. It has been used to extinguish magnesium chip fires, magnesium casting fires, molten magnesium spill fires, titanium turning fires, titanium sponge fires, titanium powder fires, and zirconium sponge fires, and also to control small sodium and sodium-potassium alloy fires.

Trimethoxyboroxine is a colorless liquid prepared by the reaction of methyl borate with boric oxide. It was first reported (*2*) by Schiff in 1867 and was assigned the formula $BO(OCH_3)$. More recently it has been designated $B_3O_3(OCH_3)_3$. Goubeau and Keller (*1*) reported the preparation and characterization of several substituted boroxines, including trimethoxyboroxine, in 1951. They cite the molecular weight and the Raman spectra as evidence for the cyclic structure shown below.



The proposed cyclic structure is isoelectronic with benzene and borazine.

The organic characteristics of this substance are particularly noticeable in its miscibility with many organic liquids. Among the compounds with which it is miscible are (Table I): phthalate esters, halogenated hydrocarbons, and triethyl phosphate, which may be of interest as components of specialty extinguishing agents.

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Table I. Solubility of Organic Liquids in Trimethoxyboroxine at 25°C.

Solute	Solubility, Grams/Ml. TMB	Remarks
Benzene	∞	
Toluene	∞	
Xylene	∞	
2,3-Dimethylbutane	0.6	Separates on cooling
n-Pentane	0.45	Separates on cooling
Ligroin	∞	Separates on cooling
Dimethyl ether	∞	
Isopropyl ether	∞	
Methyl ethyl ketone	∞	
Dimethylformamide	∞	Solution warms on mixing
Carbon disulfide	1.9	
Carbon tetrachloride	∞	Viscosity of 0.8 molal soln. = 44.6 cs. at 32°F.[a]
Chlorobromomethane	∞	Viscosity of 0.9 molal soln. = 37.1 cs. at 32°F.
Triethyl phosphate	∞	Viscosity of 1.1 molal soln. = 36.5 cs. at 32°F.
2-Ethylhexyl phthalate	∞	Viscosity of 0.1 molal soln. = 123 cs. at 32°F.

[a] Viscosity of TMB at 32°F., 122.8 cs.

In the preparation of trimethoxyboroxine for use as a metal fire extinguishing agent, sold by Callery under the trademark TBM, more emphasis has been placed on obtaining a composition of matter with a certain density and viscosity rather than a pure chemical. This is because these properties have effects on nozzle spray patterns and the emptying time of the extinguisher. Trimethoxyboroxine may be considered as a component of the system methyl borate–boric oxide. In this system the density appears to change in a regular manner with increasing total boric oxide content. The viscosity of this system increases rapidly, however, once the mole ratio of boric oxide to methyl borate exceeds 1. These relationships are shown in Figures 1 and 2. Figure 2 is a plot of viscosity *vs.* temperature on a portion of ASTM Viscosity Chart E. The

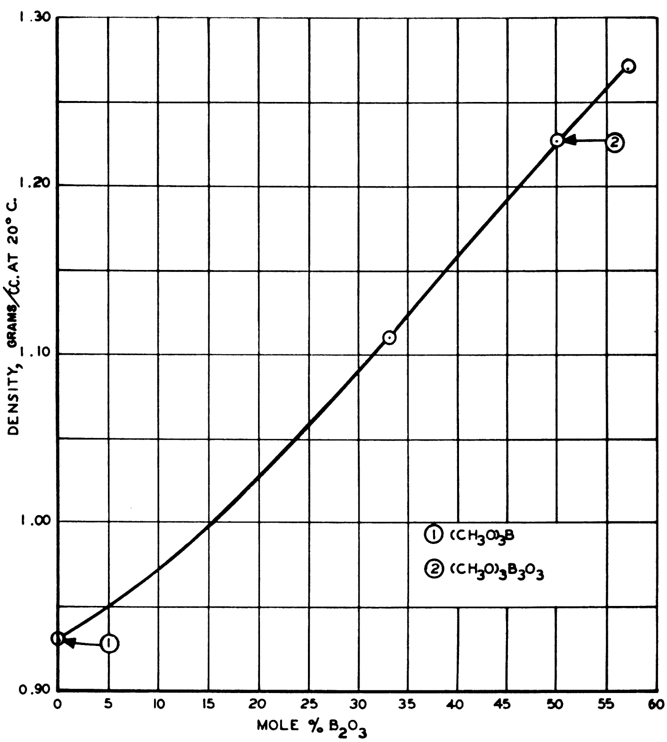


Figure 1. Density of compositions in the system boric oxide –methyl borate vs. mole per cent of boric oxide

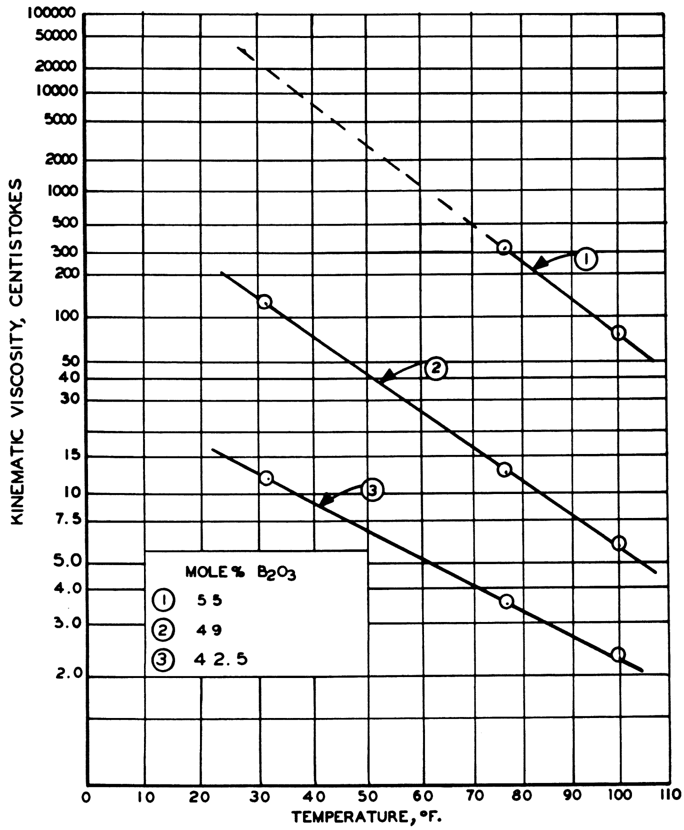


Figure 2. Viscosity of compositions in the system boric oxide –methyl borate vs. temperature

ASTM Viscosity Chart E

latter is a modified semilog paper which gives straight-line plots for the viscosities of petroleum products and other Newtonian fluids. It can be seen that trimethoxyboroxine may be considered a Newtonian fluid.

Two reactions of trimethoxyboroxine occur during its use as a metal fire extinguishing agent. Under the influence of heat, trimethoxyboroxine breaks down into methyl borate and boric oxide as shown in Equation 1. More important, boric oxide is also the principal product from the combustion of trimethoxyboroxine in air as is indicated in Equation 2.

$$B_3O_3(OCH_3)_3 \xrightarrow{120°C.} B(OCH_3)_3 + B_2O_3 \quad (1)$$

$$2B_3O_3(OCH_3)_3 + 9O_2 \longrightarrow 3B_2O_3 + 9H_2O + 3CO_2 \quad (2)$$

Metal fires are difficult to extinguish because of the great reactivity of the materials at their ignition temperatures. At these temperatures they will combine with many materials which are ordinarily considered to be relatively inert, such as nitrogen. Therefore, effective extinguishing of a metal fire is obtained only by complete exclusion of the atmosphere or by cooling the mass of the metal below its ignition temperature. These effects are usually obtained by blanketing the fire with a dry inert solid material to exclude the atmosphere or by applying an organic liquid which has a high heat of vaporization to cool the mass below the ignition temperature.

Trimethoxyboroxine, being a liquid, possesses the advantages of the organic liquid extinguishing agents in that it can be applied as a stream or a spray depending upon the conditions of the fire. The inorganic component of trimethoxyboroxine, boric oxide, which is regenerated by either thermal decomposition or combustion, is a very effective extinguishing agent. At the temperature of the burning metal, boric oxide melts to a flux which flows over the hot metal and excludes the atmosphere.

As a result of these characteristics metal fire extinguishment with trimethoxyboroxine is frequently more rapid than with other extinguishing agents, less extinguishing agent is required, and frequently more unburned metal is recoverable. In addition, the products of combustion (Equation 2) are virtually nontoxic.

In the case of chip or sponge fires, burning occurs over a considerable area and in addition penetrates within the mass. Trimethoxyboroxine should be applied over the entire area in a stream, including particularly the hottest points where the fire is progressing inward. Casting fires are characterized by intensely white spots on the surface where burning is occurring as well as by a general fire over any pools of molten metal that may have formed. Again trimethoxyboroxine should be directed towards the hottest spots in a straight stream. However, if a large molten pool is present, care should be exercised to avoid disturbing the surface. In such cases, most efficient use of trimethoxyboroxine will be obtained if it is allowed to flow over the molten fire or if it is applied as a spray.

The secondary fire from the combustion of trimethoxyboroxine is characterized by greenish flames 2 to 3 feet high. There is also a cloud of white smoke. This fire subsides quickly when the application of trimethoxyboroxine is stopped. One application of trimethoxyboroxine is usually sufficient to extinguish the metal fire. If small areas of burning material are missed, short bursts of trimethoxyboroxine will quench them rapidly. If too much trimethoxyboroxine is used, a small secondary fire with green flames 2 to 3 inches high will continue to burn for several minutes. At this point the vigorous fire may be considered out. However, the residue will be quite hot. The residue can be left to cool by itself or, in certain cases if there is the danger of igniting other flammable materials, a stream of water can be used to cool the unburned metal.

Test Fires

Several metal fires were ignited and extinguished with trimethoxyboroxine. The trimethoxyboroxine was used in standard water-type extinguishers pressurized with dry nitrogen. These extinguishers have several features which limit the effective use of trimethoxyboroxine. At present, other laboratories are working on programs to develop better equipment and techniques of application. The trimethoxyboroxine used in these tests conformed to the specifications shown in Table II.

Table II. Physical Properties of Trimethoxyboroxine

Property	Typical Product
Total % B_2O_3[a]	59.7
Specific gravity at 25°C.	1.216
Viscosity at 25°C.	13.0 cs.
Turbidity[b]	100
Pour point	−22°F.
Refractive index, n_D^{25}	1.3986
Flash point (COC)	90°F.

[a] Theoretical for trimethoxyboroxine is 60.0% boric oxide.
[b] Turbidity determined as % transmission of white light.

Broken zirconium sponge (20-mesh) was used for one fire; 4 pounds of sponge were arranged in a pyramid about 9 inches in diameter and were ignited. The fire spread rapidly over the surface. Trimethoxyboroxine was applied in a straight

stream for 10 seconds and completely extinguished the fire. Less than 0.5 gallon of trimethoxyboroxine was used. After the residue cooled, it was broken open. Under the crust of boric oxide there remained a large percentage of unburned zirconium. The residue was extremely difficult to reignite. A propane torch had to be used to burn the boric oxide from the surface of the zirconium before ignition occurred.

A titanium sponge fire was extinguished with similar results. Another fire was started with granular titanium sponge and then a block of sponge $8 \times 8 \times 8$ inches was placed on top. It ignited rapidly and the fire burned upward. Again less than 0.5 gallon of trimethoxyboroxine was sufficient to extinguish the fire. On examination of the large piece of sponge it was found that the inward penetration of the fire was halted.

Trimethoxyboroxine was applied as a straight stream to a 17-pound magnesium chip fire for 18 seconds. The fire was knocked down except for a few small spots on one side. A second short spraying for 5 seconds completely extinguished the fire. The residue was allowed to cool, then it was opened and examined. About 80% of the magnesium chips were unburned. The trimethoxyboroxine had stopped the inward penetration of the fire into the pile. Less than 0.5 gallon of trimethoxyboroxine had been used.

A 16-pound magnesium casting was ignited with 5 gallons of naphtha. After 4 minutes the casting began to melt and a minute later ignition at various spots was observed. After the fire had burned for 8 more minutes, a substantial portion of the casting had melted. The fire was burning over most of the molten area and on the casting. Trimethoxyboroxine was applied as a straight stream for 6 seconds. Then the secondary fire was allowed to die down and intermittent sprays of trimethoxyboroxine were directed at various spots. The total elapsed time was 40 seconds. Only 3.5 pounds of trimethoxyboroxine were used to extinguish the fire completely.

Trimethoxyboroxine was applied as a spray on a 12-pound sodium fire such as might occur with a spill. The fire was extinguished. However, after 2 or 3 minutes the boric oxide coating dissolved partially and small patches of the metal surface reignited. These flare-ups were extinguished with a second short spraying. A total of about 0.5 gallon of extinguishing agent was used. With fires of this type extreme care must be taken not to disturb the surface of the molten metal. If the surface is accidentally broken, the liquid metal will reignite.

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Organoaluminum Compounds

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Aluminum alkyl reactions which have possible industrial applications are discussed. Ziegler and his coworkers have outlined a new field of organic reactions, using organoaluminum compounds, which will have a tremendous impact on both basic and applied organic chemistry.

The first organoaluminum compound, trimethylaluminum, was made in 1865 by the reaction of dimethylmercury and aluminum (*3*). Subsequently, very little work was done on organoaluminum compounds until 1948 when Ziegler and his coworkers of the Max Planck Institut für Kohlenforschung started investigating them as catalysts and chemical intermediates.

The classical preparative methods using mercury dialkyls and aluminum, Grignard reagents and aluminum chloride, or ethyl chloride with aluminum and sodium are too costly for the production of aluminum alkyls on a commercial scale for use as chemical intermediates. Ziegler developed several methods for the low-cost production of aluminum trialkyls which include: reaction of an aluminum-magnesium alloy with an alkyl halide (*20, 21*),

$$Al_2 \cdot Mg_3 + 6RCl \rightarrow 2AlR_3 + 3MgCl_2 \qquad (1)$$

addition of an olefin to aluminum hydride (*16*),

$$AlH_3 + 3CH_2{=}CR_2 \rightarrow Al(CH_2CHR_2)_3 \qquad (2)$$

and reaction between aluminum, hydrogen, and an olefin (*7, 18*).

$$Al + 1.5H_2 + 3C_nH_{2n} \rightarrow Al(C_nH_{2n+1})_3 \qquad (3)$$

The last reaction is carried out readily with 1,1-disubstituted olefins such as isobutylene. Good yields of triisobutylaluminum can be made from finely divided aluminum, hydrogen, and isobutylene at 50 to 100 atmospheres and about 120°C. With ethylene and monosubstituted ethylenes, an indirect method can be used. Aluminum, hydrogen, and some previously prepared aluminum trialkyl react to form the aluminum dialkyl hydride. Then olefin is supplied which adds to the aluminum-hydrogen bond to form the trialkyl. In practice, this takes place in one step by the reaction of aluminum, an olefin, hydrogen, and an aluminum trialkyl. For example, with ethylene:

$$Al + 1.5H_2 + 2Al(C_2H_5)_3 + 3C_2H_4 \rightarrow 3Al(C_2H_5)_3 \qquad (4)$$

The triethylaluminum is acting as a catalyst for its own formation. Thus, we now have a low-cost process for preparing any aluminum trialkyl from available alpha olefins.

The lower molecular weight aluminum trialkyls are water-white liquids, specific gravity about 0.8, and are soluble in hydrocarbon solvents. The methyl and ethyl derivatives can be distilled at atmospheric pressures at 130° and 194°C., respectively. Higher members of the series can be distilled at low pressures without decomposition —e.g., triisobutylaluminum, which has a boiling point of 40°C. at 0.1 mm. of mercury pressure. The lower members are spontaneously flammable in air and on contact with water. The chemistry of aluminum trialkyls is based largely on the reactions of triethylaluminum and the higher homologs, as they are made readily from cheap raw materials.

Metal alkyls are extremely reactive chemicals. Relatively little has been published on the reactions of aluminum alkyls, and it has been only in the last few years that reactions of them have been discovered which are commercially important.

Thermal Decomposition

A typical reaction of all aluminum alkyls is their ease of thermal decomposition into metallic aluminum, an olefin, and hydrogen at elevated temperatures. This appears to involve two distinct steps as shown in Equations 5 and 6 for triisobutylaluminum (*14*):

$$Al\left(CH_2CH\begin{matrix}CH_3\\CH_3\end{matrix}\right)_3 \xrightarrow{100^\circ C.} AlH\left(CH_2CH\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2 + CH_2{=}C(CH_3)_2 \qquad (5)$$

$$AlH\left(CH_2CH\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2 \xrightarrow{>200^\circ C.} Al + 1.5H_2 + 2CH_2{=}C(CH_3)_2 \qquad (6)$$

Compounds in which the alkyls are straight-chained radicals are much more stable than those in which branching occurs on the second carbon atom. Trimethylaluminum and triethylaluminum can be distilled without decomposition at atmospheric pressure and do not break down until relatively high temperatures are reached. Triisobutylaluminum and similar alkyls lose 1 mole of olefin at 100°C. to form the monohydride. The monohydride is stable up to about 200°C. and then breaks down completely (Equation 6).

These reactions show some promise of having commercial application where it is desired to deposit films of aluminum on metal and nonmetallic surfaces. This can be done in two ways. Glass and metallic surfaces may be coated by passing vapors of triisobutylaluminum over such surfaces while heating them to about 250°C. This must be done at reduced pressures because the triisobutylaluminum cannot be distilled successfully above 10 mm. The same result is produced by first making diisobutylaluminum hydride, into which the object to be coated is dipped, and subsequently heating to about 250°C. In either case, aluminum is deposited, and isobutylene and hydrogen are formed and must be swept away. This decomposition can be used to prepare very pure aluminum by first treating finely divided, activated aluminum which is relatively impure with isobutylene and hydrogen to form the alkyl. Then the alkyl is decomposed to form very pure aluminum (*11*).

Reaction with Active Hydrogen

Another typical reaction of aluminum alkyls and all metal alkyls is their action with active hydrogen such as that contained in water, acids, and alcohols.

$$AlR_3 + 3HX \rightarrow AlX_3 + 3RH \qquad (7)$$

In this case a saturated hydrocarbon is formed, and the aluminum appears as aluminum alcoholate, aluminum hydroxide, or an aluminum salt.

This reaction could be used to convert olefins to saturated hydrocarbons, but it is not a commercially attractive substitute for hydrogenation. As it is responsible for most of the losses of aluminum alkyls in ordinary chemical manipulations, it necessitates careful purification of olefins and other reagents which are used in connection with aluminum alkyl reactions.

Oxidation

A characteristic reaction of aluminum alkyls is the formation of aluminum alcoholates on treatment with oxygen (*14*).

$$AlR_3 + 1.5O_2 \rightarrow Al(OR)_3 \quad (8)$$

This reaction shows promise as a process for producing primary alcohols from commercially available terminal olefins. It is necessary only to make the appropriate aluminum alkyl, oxidize it to the alkoxide, and then hydrolyze this to aluminum hydroxide and the corresponding alcohol, which is always primary.

Olefin Displacement

A general reaction of aluminum alkyls is the reaction in which one olefin can displace another to produce a new alkyl and an olefin. This reaction enables one to prepare easily any aluminum alkyl from the appropriate olefin and triisobutylaluminum (*14*), the most easily prepared aluminum alkyl.

$$Al\left(CH_2CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right)_3 + 3CH_2{=}C\begin{matrix} R \\ R' \end{matrix} \xrightarrow{100° \text{ to } 120°C.} Al\left(CH_2CH\begin{matrix} R \\ R' \end{matrix}\right)_3 + 3CH_2{=}C(CH_3)_2 \quad (9)$$

where R and R′ can be either hydrogen or another alkyl radical.

This reaction may have commercial application in preparing alcohols from certain petroleum refinery olefin streams. If triisobutylaluminum reacts with the alpha olefins in the refinery stream at about 100° to 120°C., a new aluminum alkyl and isobutylene are produced. The unreacted olefins or hydrocarbons can be distilled, and the remaining aluminum alkyl is oxidized and hydrolyzed to produce an alcohol and aluminum hydroxide. In an alternative method, the olefin reacts with hydrogen and suitably activated aluminum to produce the alkyl, which can then be converted to an alcohol. Thus, 2-phenylethyl alcohol could be prepared from styrene, a primary alcohol from triisobutylene, or a primary terpene alcohol from limonene (*14*).

Reducing Properties

Aluminum alkyls, particularly triisobutylaluminum and diisobutylaluminum hydride, are very good reducing agents for carbonyl groups in aldehydes, ketones, and esters. Alcohols are formed, and the aluminum alkyl appears to act like lithium aluminum hydride except that the total reducing capacity is not always utilized. Although this reagent may be less efficient than lithium aluminum hydride on a molar basis, the low cost of triisobutylaluminum more than compensates for this inefficiency (*14*).

Use as a Grignard Reagent

Ordinarily, the use of an aluminum alkyl compound as a Grignard reagent with carbonyl groups results in reduction. In certain cases Grignard-like addition takes place, but only one of the aluminum alkyl bonds is involved. The formation of the first $R_2Al—O—$ bond seems to inactivate the other two bonds (*14*).

Reactions with Halogens and Sulfur Dioxide

Halogens react with trialkyl aluminum compounds to produce an aluminum salt and a primary halide (*10*):

$$AlR_3 + 3X_2 \rightarrow AlX_3 + 3RX \quad (10)$$

Sulfur dioxide adds aluminum alkyls to form salts of sulfinic acids (*10*):

$$AlR_3 + 3SO_2 \rightarrow Al(SO_2R)_3 \quad (11)$$

Reaction with Metal Salts

Salts of metals which can form stable metal alkyls react with aluminum alkyls to produce the expected metal alkyl and an aluminum salt (*10*):

$$2AlR_3 + 3CdCl_2 \rightarrow 2AlCl_3 + 3CdR_2 \quad (12)$$

$$AlR_3 + 2HgCl_2 \rightarrow AlCl_3 + HgR_2 + HgRCl \quad (13)$$

$$AlR_3 + BF_3 \rightarrow AlF_3 + BR_3 \quad (14)$$

$$xAlR_3 + xSiF_4 \rightarrow SiF_3R + SiF_2R_2 + SiFR_3 + SiR_4 + AlF_3 \quad (15)$$

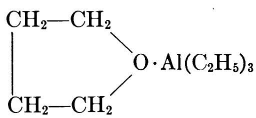
The last reaction can be controlled to produce largely SiF_2R_2 and SiF_3R which may have some application to silicon chemistry. Hydrolysis would yield $SiR_2(OH)_2$ and $SiR(OH)_3$, which could be condensed to silicones. This process has been developed by Kali-Chemie A.-G. in Germany (*5*).

Formation of Complex Salts

Another characteristic reaction of aluminum alkyls is the formation of complex salts with a variety of organic and inorganic compounds (*2*). The following are examples of such complexes:

$(C_2H_5)_2O \cdot Al(C_2H_5)_3$

$(CH_3)_2N \cdot C_6H_{11} \cdot Al(C_2H_5)_3$



$C_5H_5N \cdot Al(C_2H_5)_3$

$(CH_3)_2NC_6H_5 \cdot Al(C_2H_5)_3$

Quinoline $\cdot Al(C_2H_5)_3$

Very little is known about the properties of such complexes as catalysts or as reagents.

Of greater interest are those complexes formed with alkali metal salts (*14*).

$$Al(C_2H_5)_3 + NaF \rightarrow NaF \cdot Al(C_2H_5)_3 \quad (16)$$

$$2Al(C_2H_5)_3 + NaF \rightarrow NaF \cdot 2Al(C_2H_5)_3 \quad (17)$$

The 1 to 1 complex melts at 74°C., whereas the 1 to 2 complex is liquid at room temperature and conducts electricity well. Practically all of the aluminum alkyls form such complex salts with sodium fluoride and potassium fluoride.

These complex salts of aluminum alkyls appear to have an interesting future as

electrolytes for use in the electroplating of metal objects with aluminum (*9*). Up to now, no practical process for electroplating aluminum is known. A process based on molten inorganic salts has worked fairly well on a laboratory scale, but some difficult engineering problems need solving before large-scale operation is possible. The sodium fluoride–aluminum alkyl complex salts are essentially molten salt electrolytes which are liquid below 100°C. As it is possible to plate aluminum on copper wire (*9*), developments are in progress to extend this process to the coating of thin sheet steel such as is used in making containers.

Another potential use for these salts from triethylaluminum is in the synthesis of tetraethyllead. The complex salt is used as an electrolyte with a lead anode and an aluminum cathode. Passage of current through the cell forms tetraethyllead, which drips off the anode, and pure aluminum, depositing at the cathode in a finely divided form (*14*).

$$NaF \cdot Al(C_2H_5)_3 + \tfrac{3}{4}Pb \rightarrow \tfrac{3}{4}Pb(C_2H_5)_4 + Al + NaF \qquad (18)$$

Triethylaluminum must be added to replenish the bath as the reaction progresses. Considering the methods available for making triethylaluminum, tetraethyllead is made essentially from ethylene, hydrogen, and lead metal. This process is being studied to determine its value in comparison with the present commercial process.

Reaction with Metals and Hydrogen

A recent patent describes the preparation of other metal alkyls from an aluminum trialkyl, a metal, and hydrogen. Thus with lead and hydrogen, triethylaluminum produces tetraethyllead and aluminum hydride (*1*).

$$4Al(C_2H_5)_3 + 6H_2 + 3Pb \rightarrow 4AlH_3 + 3Pb(C_2H_5)_4 \qquad (19)$$

Adding ethylene to the aluminum hydride will reform triethylaluminum which can be re-used.

Growth Reaction

Aluminum trialkyl compounds, except those made from isobutylene or similar olefins, can add ethylene to form higher alkyls or grow. This is an important reaction of aluminum alkyls. Control of the reaction conditions enables preparation of higher aluminum alkyls which can be used to produce saturated hydrocarbons, olefins, or alcohols.

If ethylene is passed into triethylaluminum at a temperature of about 200°C. at atmospheric pressure, 1-butene is formed together with very small amounts of 1-hexene and 1-octene (*14, 16*):

$$xCH_2{=}CH_2 \xrightarrow[Al(C_2H_5)_3]{200°C.} CH_2{=}CH{-}C_2H_5 + CH_2{=}CH{-}C_4H_9 + CH_2{=}CH{-}C_6H_{13} \qquad (20)$$

Actually the primary products are the corresponding alkyls and the over-all reaction is:

$$Al(C_2H_5)_3 + 3CH_2{=}CH_2 \rightarrow Al(CH_2CH_2CH_2CH_3)_3 \qquad (21)$$

then,

$$Al(CH_2CH_2CH_2CH_3)_3 + 3CH_2{=}CH_2 \xrightarrow{200°C.} CH_2{=}CH{-}C_2H_5 + Al(C_2H_5)_3 \qquad (22)$$

The nature of the product is determined by the pressure of ethylene, the time of contact, and the temperature. Under the conditions cited above, only relatively low molecular weight olefins are formed. Occasionally, small amounts of olefins are formed where the double bond has moved toward the center of the molecule. This can be minimized by using short contact times and small amounts of phenylacetylene

(ethynylbenzene) to inhibit the migration. The optimum conditions for producing 1-butene by this process involve passing ethylene at 40 atmospheres into triethylaluminum at 100° to 110°C. containing a small amount of colloidal nickel and 0.5% of phenylacetylene (*13*).

If propylene is used instead of ethylene, the propylene dimer is formed exclusively and quantitatively:

$$2CH_2{=}CHCH_3 \xrightarrow[Al(C_2H_5)_3]{200°C.} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C_3H_7 \qquad (23)$$

At first the small amount of ethylene is displaced by the incoming propylene and swept out of the system leaving tripropylaluminum which is the real catalyst. Higher polymers of propylene are not formed. Apparently, aluminum alkyls in which the second carbon from the metal has a branch cannot add other olefins, even ethylene. Instead, if the temperature is high enough, they react by splitting out the branched olefin. If another olefin is present which can form an unbranched alkyl, a new alkyl is formed. With propylene, 2-methyl-1-pentene is split out and tripropylaluminum is formed which again reacts with more propylene. This process can be applied to 1-butene, 1-pentene, and others with almost equal results.

Codimerization of different olefins is possible but usually results in a mixture of all possible products.

Ziegler's work on the dimerization reaction resulted in a process for synthesizing *p*-xylene from ethylene. The reactions involved are (*6*):

$$2CH_2{=}CH_2 \xrightarrow[Al(C_2H_5)_3+Ni+0.5\%\ C_6H_5{-}C{\equiv}CH]{40\ atm.\ 110°C.} CH_2{=}CHCH_2CH_3 \qquad (24)$$

$$2CH_2{=}CHCH_2CH_3 \xrightarrow[Al(C_2H_5)_3]{200°C.} CH_2{=}\underset{\displaystyle C_2H_5}{\underset{|}{C}}CH_2CH_2CH_2CH_3 \qquad (25)$$

$$CH_2{=}\underset{\displaystyle C_2H_5}{\underset{|}{C}}CH_2CH_2CH_2CH_3 \xrightarrow[Cr_2O_3]{500°C.} 55\%\ p\text{-xylene} + 26\%\ o\text{-xylene} + 19\%\ \text{ethylbenzene} \qquad (26)$$

The product of the first step is substantially pure 1-butene and excess ethylene. From the second step, only 2-ethyl-1-hexene and unchanged 1-butene are obtained. The aromatization reaction uses a conventional chromite catalyst. The final product is separated easily into its components by fractional distillation and crystallization. Cost calculations showed that *p*-xylene made by this process was cheaper than that available at the time, but it was not cheap enough to compete with predicted future prices for *p*-xylene made by other methods from petroleum.

The growth reaction can be extended to produce high molecular weight alkyls and from these the corresponding olefins and alcohols. For this reaction, higher pressures of ethylene and longer contact times are required at temperatures below those at which olefins are displaced. Typical conditions are ethylene pressures of 100 or more atmospheres at 100° to 150°C. for 1 or more hours. Under such conditions, the reaction (*14*) is similar to Equation 27:

$$Al(C_2H_5)_3 + xCH_2{=}CH_2 \xrightarrow[100°C.]{100\ atm.} Al\begin{matrix}(CH_2{-}CH_2)_m{-}C_2H_5\\(CH_2{-}CH_2)_n{-}C_2H_5\\(CH_2{-}CH_2)_o{-}C_2H_5\end{matrix} \qquad (27)$$

The product is always a mixture of aluminum alkyls, but the average length of the alkyl chain apparently can be peaked somewhat by regulating the conditions.

A typical reaction, in which 6 moles of ethylene reacted for each mole of triethylaluminum used, gave a product in which the alkyl chains were distributed as in Table I. The last column gives the weight–per cent distribution of a product which

Table I. Distribution of Reaction Products

	Mole %	Wt. %	Wt. % as ROH
C_2H_5	15	5.0	7.0
C_4H_9	26	18.0	19.0
C_6H_{13}	27	27.5	27.5
C_8H_{17}	17	23.0	22.0
$C_{10}H_{21}$	9	15.0	14.0
$C_{12}H_{25}$	4	8.0	7.5
$C_{14}H_{29}$	1	2.5	2.0
$C_{16}H_{33}$	1	1.0	1.0

would be obtained by oxidation of the alkyls followed by hydrolysis of the alcoholates. In addition to producing alcohols, these alkyls could be used to make normal olefins by displacement, or normal paraffins by hydrolysis. Because the successive members of the series differ by two carbon atoms, the mixture of products can be separated into fairly pure compounds by fractional distillation.

The growth reaction followed by hydrolysis, thermal decomposition, or oxidation and hydrolysis provides an attractive means for synthesizing straight-chained saturated hydrocarbons, olefins, and alcohols. No significant commercial uses are known for these hydrocarbons or olefins. The alcohols have many important applications. The process is probably too costly for making alcohols with six carbon atoms or less. Because material costs drop as carbon content increases, it appears very attractive for preparing alcohols in the 10- to 14-carbon range: Less of the expensive aluminum metal is consumed as the chain length increases.

Continued investigation of the growth reaction showed that it could be used to prepare olefins with molecular weights as high as 5000 (*17*). This was done by using a large excess of ethylene and pressures up to several thousand pounds. These higher molecular weight products ranged from soft low-melting to very hard high-melting waxes. It was not possible to prepare polyethylene with plastic-range molecular weights at moderate pressures by the simple growth reaction from triethylaluminum and ethylene. However, Ziegler observed the profound effect of small quantities of certain metal salts on the growth reaction, which led to his process for preparing plastic-grade polyethylene at low pressures.

Ziegler discovered that a catalyst, composed of an aluminum trialkyl and small amounts of a transition metal salt such as titanium tetrachloride, was capable of polymerizing ethylene at low pressure to a very high molecular weight product at 50° to 100°C. (*8*):

$$xCH_2{=}CH_2 \xrightarrow{1\%\ (AlR_3+TiCl_4)} (-CH_2-CH_2-)_x \qquad (28)$$

where x can be varied from 1000 to 400,000. As in the growth reaction, the ethylene had to be very free from active impurities like oxygen, water, sulfur, and acetylene, but did not require the absence of inert materials like saturated hydrocarbons and nitrogen. In most cases, the reaction was carried out in an inert hydrocarbon solvent such as Diesel oil. A wide variety of organometallic compounds such as aluminum dialkyl halides, zinc alkyls, and sodium aluminum alkyls can be used in place of the trialkylaluminum. Apparently, any of the transition metal salts could be used in place of titanium tetrachloride. Ziegler's work covered the use of salts of zirconium, hafnium, vanadium, tantalum, and chromium (*8*).

He found that the molecular weight of the product could be varied at will and seemed to be controlled by the ratio of aluminum alkyl to transition metal salt in the catalyst (*12*). This is illustrated in Table II. A high molecular weight product in the range of 300,000 resulted if the aluminum alkyl to titanium salt mole ratio was 12 to 1. The molecular weight of the product did not change much as the mole ratio of aluminum alkyl to titanium salt dropped until a value from 0.5 to 1 was reached. With this catalyst composition, the molecular weight dropped to 20,000 (*12*).

This type of catalyst system can be used to polymerize practically any alpha olefin from propylene to styrene, and probably beyond, to yield either amorphous

Table II. Effect of Catalyst Composition on Molecular Weight

Molar Ratio, AlR_3 to $TiCl_4$	4-Hr. Yield, Grams	Av. Mol. Wt.
12	440	272,000
6	430	292,000
3	460	298,000
1	440	284,000
0.63	480	160,000
0.53	460	40,000
0.50	300	21,000
0.20	10	31,000

or crystalline polymers and sometimes a mixture of both (*19*). Apparently, different monomers can be copolymerized. In practically all cases, the reaction rate is slower than for ethylene at a given temperature and pressure. With propylene, under certain conditions, the polymer obtained was a mixture of amorphous and crystalline material. By a suitable extraction procedure, an amorphous rubber fraction with a molecular weight of less than 45,000 was separated. The residue from such an extraction was a crystalline solid which melted at 100° to 150°C. and had a molecular weight above 100,000. The crystalline fraction could be extruded into filaments and stretch-oriented to form products with very high tensile strength. Crystalline polystyrene also has been made with a molecular weight above 2,800,000, a density of 1.08, and a softening point above 200°C. (*19*).

A large rubber company announced the use of Ziegler-type catalysts to polymerize isoprene to a rubber which is apparently identical with natural rubber (*4*), as shown by infrared absorption and x-ray diffraction data. Physical properties and the results of field tests further substantiate this.

Summary

It is difficult to tell which of Ziegler's many reactions will be the most important. Certainly, the low pressure synthesis of polyethylene is most important to industry. Probably the most notable reactions are: the synthesis of aluminum alkyls from olefins, hydrogen, and aluminum; the growth of long unbranched aliphatic chains from aluminum alkyls and ethylene and their use to make saturated hydrocarbons, olefins, and alcohols; and the synthesis of high polymers of ethylene and other olefins at low pressures using a catalyst composed of aluminum alkyls and transition metal salts.

Future workers should expand the applications of these reactions and also discover many more.

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Preparation and Ignition Properties of Aluminum Alkyls

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Three years ago, a joint project was established by the Wright Aeronautical Division, Curtiss-Wright Corp., at the Jet and Flame Laboratory of New York University, to study the preparation and behavior of pyrophoric organometallic compounds. The aluminum alkyls have been one of the most interesting groups studied to date, from an ignition standpoint.

Compounds capable of ready spontaneous ignition with air are of considerable potential importance for certain types of air-breathing power plants. Certain thermal theories of flame propagation suggest that the flame is propagated by virtue of continuous spontaneous ignition occurring on the leading edge of the flame front; in such a case, the time lapse before the flame appears—ignition delay—would be an important factor.

Although aluminum alkyls have been known for some time, it has been only during the past few years that these compounds have been the subject of extensive research, largely because of the use of these compounds by Ziegler as catalysts for olefin polymerizations at low pressures.

Preparation of Aluminum Alkyls

A convenient method for the preparation of small quantities of these compounds involves a displacement reaction between aluminum metal and the alkyl compound of some less active metal (which can be readily prepared)—e.g., the reaction of dimethylmercury with an excess of aluminum yields trimethylaluminum and mercury (*2*):

$$2Al + 3(CH_3)_2Hg \rightarrow 2(CH_3)_3Al + 3Hg$$

Although this procedure gives good yields for lower members of the series, the decreased stability of the higher mercury alkyls limits its usefulness. The cost of such a method would be high.

Recently Ziegler has developed several new methods of preparing aluminum alkyls using olefins as the starting reagents (*10, 11*). At about 100° C. lithium aluminum hydride reacts with ethylene and tetraethylaluminum lithium is formed:

$$LiAlH_4 + 4C_2H_4 \rightarrow LiAl(C_2H_5)_4$$

When this quaternary salt is treated with aluminum chloride, triethylaluminum is formed:

$$3LiAl(C_2H_5)_4 + AlCl_3 \rightarrow 3LiCl + 4Al(C_2H_5)_3$$

This method has been used to prepare the corresponding *n*-propyl and *n*-hexyl compounds.

A more economical process for the large scale production of these compounds involves spraying aluminum into an atmosphere of hydrogen and an olefin (*12*):

$$Al + 3C_2H_4 + 3/2H_2 \rightarrow Al(C_2H_5)_3$$

$$Al + 3CH_2{=}C\begin{matrix}CH_3\\ CH_3\end{matrix} + 3/2H_2 \rightarrow \left(\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH{-}CH_2\right)_3 Al$$

Alkyl aluminum hydrides may be formed by adjusting the proportions of the reactants:

$$2R_3Al + Al + 3/2H_2 \rightarrow 3R_2AlH$$

It is evident that trimethylaluminum, the simplest member of the series, and the one which is of most interest in this study, cannot be made by the reactions which involve the use of olefins as starting materials. To prepare this compound one can employ the general reaction of an alkyl halide and aluminum, which results in the formation of an equimolar mixture of the monoalkylaluminum dihalide and dialkylaluminum monohalide called a sesquihalide:

$$2Al + 3RX \rightarrow R_2AlX + RAlX_2$$

In general, the sesquiiodides readily disproportionate on heating, and trimethylaluminum may be prepared by heating methylaluminum sesquiiodide and removing the most volatile component, trimethylaluminum, from the top of a fractionating column (*8*). This convenient method for preparing trimethylaluminum was initially used in these laboratories for the preparation of pound quantities of this compound.

Preparation of Trimethylaluminum from Methyl Iodide and Aluminum. Trimethylaluminum, triethylaluminum, and some of their halides are extremely reactive substances which are spontaneously flammable in air and react with water with explosive violence. Care must be taken that all apparatus is completely dry before starting any experiments. It is also important that apparatus be selected in which there is little possibility for the development of air leaks. By far the most annoying difficulty encountered in these laboratories was the development of air leaks during the fractionation step, because aluminum oxide can deposit in the column and it may become plugged.

Aluminum turnings (4 pounds) are placed in a 12-liter glass flask attached to the bottom of an efficient fractionating column. Methyl iodide (2 pounds) is introduced, and the mixture is refluxed by external heating until the reaction becomes spontaneous, as evidenced by a sudden increase in temperature in the reaction flask and by blackening of the aluminum surface. (The initiation of this reaction may be hastened by adding a small amount of the product obtained from a previous reaction or by the addition of iodine or of aluminum chloride.) The remainder of the methyl iodide (23 pounds) is then added at a rate sufficient to maintain a pot temperature of about 160° F., with external heat being required only occasionally in the late stages of the reaction. This reaction is slow and addition times of 24 to 48 hours were not uncommon.

When the reaction is complete, the mixture is distilled through a 6-foot column packed with protruded stainless steel packing. The reflux ratio is adjusted to maintain a head temperature below 72° C. at 100 mm. of mercury pressure, and varies from 4 to 1 at the beginning of the distillation to about 19 to 1 at the end of the distillation. The trimethylaluminum is a colorless liquid, boiling at 69° to 72° C. at 100 mm. and is obtained in yields of 50 to 65% of theory (about 2.5 pounds).

Two obvious disadvantages of the above procedure are the cost of the starting reagent methyl iodide, and the relatively long time required for the slow distillation and equilibration which is necessary in order to obtain a pure product.

An obvious improvement over this procedure would involve the substitution of methyl chloride for the more expensive methyl iodide. Methylaluminum sesquichloride can readily be prepared from methyl chloride and aluminum foil, which allows a large surface area for a given weight of metal.

Preparation of Methylaluminum Sesquichloride. In a dry 2-liter, three-necked flask fitted with a condenser, mercury-seal stirrer, inlet for gases, and thermometer, are placed 320 grams of aluminum foil (household grade), which has been cut into small pieces. The thermometer should extend 2 or 3 inches into the flask, in order to measure the vapor temperatures over the reacting mass. A schematic diagram of the apparatus is presented in Figure 1. A crystal of iodine is placed in the flask, which is

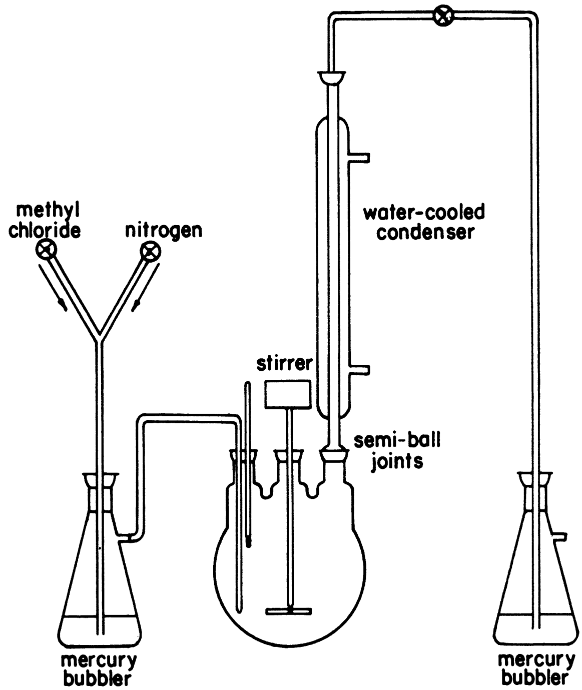


Figure 1. Apparatus for preparation of aluminum alkyls

then flushed with methyl chloride. To initiate the reaction, 5 or 6 ml. of methyl iodide are introduced into the flask through the condenser. The flask is then heated until the reaction starts, and a sudden rise in temperature to 150° C. is noted. The source of heat is removed, and the reaction continues until the methyl iodide is consumed; this takes about ½ hour. The addition of methyl chloride is begun and continued at a rate which maintains a pressure, within the system, equal to or slightly greater than atmospheric pressure. Mercury bubblers before and after the system will give a qualitative measure of the rate of passage of methyl chloride into and out of the reaction flask. The reaction is sustained by its own heat, and the temperature should be kept between 90° and 120° C. The addition of methyl chloride is stopped when its absorption no longer occurs at a reasonable rate—this requires about 20 hours. The mass is now entirely liquid, and no aluminum metal remains. The yield of methylaluminum sesquichloride is quantitative (based on aluminum).

(Note. The above procedure has also been used in these laboratories for the preparation of ethylaluminum sesquichloride.)

This product (methylaluminum sesquichloride) does not readily disproportionate, and trimethylaluminum cannot be obtained as in the case of the sesquiiodide. There are several alternative routes for the conversion of the sesquichloride to trimethylaluminum. These include:

Reduction of the sesquichloride with sodium metal.

Separation of dimethylaluminum chloride from methylaluminum dichloride through the formation of the nonvolatile complex $CH_3AlCl_2 \cdot NaCl$ with the subsequent reduction of dimethylaluminum chloride with sodium.

Conversion of the sesquichloride to dimethylaluminum chloride by the addition of one mole of trimethylaluminum to one mole of the sesquichloride, and subsequent reduction with sodium of the dimethylaluminum chloride.

Reduction of the sesquichloride with metallic sodium appears to occur according to the following equation (*5*):

$$3Na + MeAlCl_2 + Me_2AlCl_3 \rightarrow Me_3Al + Al + 3NaCl$$

In practice, the reaction is somewhat sluggish, and it appears that the formation of a complex between sodium chloride and methylaluminum dichloride causes some decrease in yields.

The fact that methylaluminum dichloride forms a nonvolatile complex with sodium chloride, while dimethylaluminum chloride does not, is used as the basis for the following separation.

Separation of Dimethylaluminum Chloride from Methylaluminum Dichloride. To the sesquichloride obtained from 320 grams of aluminum are added 450 grams of dry sodium chloride, and the mass is stirred and allowed to reflux (external heating if necessary) for 2 hours. The flask is allowed to cool, and the apparatus is arranged for distillation. The product, dimethylaluminum chloride, distills at 126–7° C. at atmospheric pressure, and weighs 460 grams (83% of the theoretical based on aluminum).

Dimethylaluminum chloride can be converted to trimethylaluminum by a single distillation with sodium.

Preparation of Trimethylaluminum from Dimethylaluminum Chloride. To a 500-ml., three-necked flask fitted with a reflux condenser and a mercury seal stirrer, are added 27 grams of sodium. The apparatus is flushed with nitrogen and 100 grams of dimethylaluminum chloride are pumped into the flask. The mixture is gently heated with slow stirring until the reaction starts; this occurs when the vapor temperature range is 95° to 100° C. The reaction is exothermic, and care must be taken to keep the reaction under control. If the reaction becomes too vigorous, stirring should be stopped and the flask cooled. The mixture is allowed to reflux for 5 hours. The chloride-free product which distills at 127° to 130° C. weighs 45 grams (90% of theory).

Triethylaluminum has also been prepared in good yields by the above procedure.

The third alternative process has not been investigated in these laboratories, but should offer considerable merit for the large-scale production of trimethylaluminum. It has been reported that the addition of triethylaluminum to ethylaluminum sesquichloride results in the formation of diethylaluminum chloride (*5*).

$$(C_2H_5)_2AlCl + C_2H_5AlCl_2 + (C_2H_5)_3Al \rightarrow 3(C_2H_5)_2AlCl$$

If such a reaction occurs with the methyl compounds, it would offer a reasonable method for the preparation of dimethylaluminum chloride, which could easily be converted to trimethylaluminum.

In the New York University laboratories dimethylaluminum chloride has been produced by the reaction of methyl chloride with an alloy of aluminum and magnesium. This is an extension of the work of Grosse and Mavity (*5*) who prepared diethylaluminum bromide from ethyl bromide and Magnalium, an alloy consisting of 70% aluminum and 30% magnesium. When methyl chloride is allowed to react with an alloy consisting of 70% aluminum and 30% magnesium, dimethylaluminum chloride

and magnesium chloride are formed. Thus, dimethylaluminum chloride can be formed by a one-step synthesis.

$$4CH_3Cl + Al_2Mg \rightarrow 2(CH_3)_2AlCl + MgCl_2$$

Preparation of Dimethylaluminum Chloride. The apparatus is similar to that used for the preparation of methylaluminum sesquichloride.

Turnings of Al_2Mg (60 grams) are placed in a 500-ml., three-necked flask. (At the time of this work, this alloy could not be obtained from a commercial source. It was prepared by the Department of Metallurgical Engineering of New York University.) A small amount of methyl iodide is introduced, in order to start the reaction, which is then allowed to continue through the addition of methyl chloride. The reaction mass slowly changes from a solid to a gray sludge as the reaction proceeds.

This reaction is slower than the one using pure aluminum, and usually requires external heating to maintain a temperature in the range of 90° to 120° C.; the reaction is complete in about 30 hours. Distillation at atmospheric pressure yields 113 grams (80%) of dimethylaluminum chloride boiling at 126–27° C. The time required for the reaction to go to completion increases appreciably as the batch size is increased.

Preparation of dimethylaluminum chloride by this procedure is slow, and requires the use of an alloy which, when available, is somewhat more expensive than pure aluminum. For these reasons it appears that the methods which utilize the sesquichloride as an intermediate are more attractive for the large-scale production of trimethylaluminum.

For the sake of convenience the physical constants of the methyl and ethyl aluminum alkyls and chloro intermediates are summarized in Table I.

Table I. Physical Constants of Methyl and Ethyl Aluminum Alkyls and Their Chloro Intermediates

Compound	Boiling Point, °C.	Melting Point, °C.	d_4^{20}, G./Cc.
Aluminum chloride, $AlCl_3$	182.7 at 752 mm., sublimes at 177.8 (Handbook of Chemistry and Physics)	194 at 5.2 mm.	2.44
Methyl aluminum dichloride, CH_3AlCl_2	97–101 at 100 mm. (*4*)	72.7 (*4*)	...
Dimethyl aluminum chloride, $(CH_3)_2AlCl$	83–4 at 200 mm. (*4*) 70–6 at 100 mm. (*4*) 58–60 at 20 mm.	Below −50	1.00
Trimethyl aluminum, $(CH_3)_3Al$	125–6 at 755 mm. (*4*)	15	0.752
Ethyl aluminum dichloride, $C_2H_5AlCl_2$	114.5–15.5 at 50 mm. (*4*)	32 (*4*)	...
Diethyl aluminum chloride, $(C_2H_5)_2AlCl$	125–6 at 50 mm. (*4*) 105–7 at 20 mm.	Below −50	...
Triethyl aluminum, $(C_2H_5)_3Al$	128–30 at 50 mm.	Below −18 −19.8	0.837

Where no reference is listed, values were determined in this laboratory.

Thermal Stabilities of Aluminum Alkyls

To measure the thermal stabilities of trimethylaluminum and triethylaluminum, two series of tests were conducted.

In the first series, a 103-ml. stainless steel cylinder connected to a pressure gage and valve system for introducing a nitrogen atmosphere was used as a constant volume container. About 1 gram of sample was introduced into the cylinder in a scaled glass vial; the cylinder was then evacuated and filled with nitrogen to a pressure of 300 p.s.i.a. The vial was broken by shaking the cylinder, and the cylinder was placed in a heating bath at the desired temperature. Temperature and pressure readings were taken at definite time intervals, and finally the pressure of the system, after cooling to room temperature, was recorded. The results of these tests are summarized in Table II.

Table II. Thermal Stabilities of Trimethylaluminum and Triethylaluminum

Compound	Conditions	Results
$Al(CH_3)_3$	300° F. for 2 hours	No evident decomposition
$Al(CH_3)_3$	450° F. for 6 hours	25 p.s.i. pressure increase; about 30% decomposition; pyrophoric residue
$Al(C_2H_5)_3$	300° F. for 2 hours	No evident decomposition

The procedure involved in the second series of tests was the same as that described above, but in this case the vials were not broken (Figure 2). Tube *B* is a

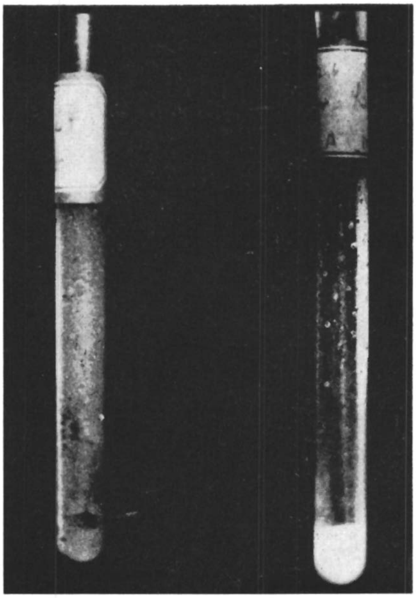


Figure 2. Thermal stability of trimethyl aluminum

Carius combustion tube that contained a 1-ml. sample of trimethylaluminum which was heated at 450° F. for 4 hours. A yellow solid was formed; the solid was shown to be aluminum carbide. Tube *A* is a similar combustion tube that contained a 1-ml. sample of triethylaluminum which was subjected to similar conditions. In this case no liquid remained, and it appears that the solid contained metallic aluminum.

Compatibilities with Materials of Construction

During this investigation, a number of tests were made to ascertain whether the aluminum alkyls are compatible with certain materials of construction. In general, most of the tests were made at room temperature, but in certain cases tests were run at elevated temperatures. The tests involved immersing samples of the materials in trimethylaluminum for varying periods of time, after which the trimethylaluminum was removed from the test flask; the samples were washed several times with benzene and/or carbon tetrachloride, removed, examined, and compared with the original material. The results of many of these tests are summarized in Tables III and IV.

From the data listed in Tables III and IV it is evident that aluminum, copper, and carbon steel are not affected by contact with trimethylaluminum at room temperature, and it has been observed that silver solder, lead, brass, and stainless steel do not react to any appreciable extent.

Most of the rubbers and their substitutes react, to some degree, with trimethylaluminum. This is not surprising, for metal alkyls are very reactive compounds which react with unsaturated groups and groups which contain active hydrogens. It is expected, therefore, that trimethylaluminum would react with olefinic groups, carbonyl groups, primary and secondary amino groups, and hydroxyl groups; because trimethylaluminum can be considered to be a Lewis acid, it can complex with basic

Table III. Effect of Immersing Certain Materials in Trimethylaluminum at Room Temperature

Material	Exposure Period, Days	Condition after Exposure
Cast iron	21	No apparent effect
Tungsten	21	No apparent effect
Molybdenum	21	No apparent effect
Zinc	21	No apparent effect
Aluminum	10	No apparent effect
Copper	10	No apparent effect
Carbon steel	10	No apparent effect
Celanese polyethylene	10	No apparent effect
U. S. Rubber polyacrylate, Style 9271	10	Surface hardened and cracked
U. S. Rubber Paracril 18-80	1	Loses elasticity, breaks easily
Du Pont Neoprene GN	35	Slight surface cracking, retains elasticity
Du Pont Neoprene W	35	Tears easily, some loss of elasticity
Enjay butyl rubber GR-1-18	19	Very soft, spongy
Enjay butyl rubber GR-1-25	19	Very soft, spongy, blistered
Enjay butyl rubber GR-1-35	19	Swollen, very spongy
Du Pont Hypalon magnesium oxide cure	35	Surface cracks, somewhat elastic
Du Pont Hypalon litharge cure	35	Cracks on bending, slightly elastic
Dow Corning Silastic 250	1	Disintegrates
Du Pont Mylar	1	Dissolves
Du Pont silicon rubbers	1	Disintegrates
U. S. Rubber 565 R	7	Blisters
U. S. Rubber 575	7	Hardens and blisters
U. S. Rubber cured Neoprene 3077	7	Blisters and hardens
U. S. Rubber 566R	7	Hardens
U. S. Rubber 3048	7	Hardens, cracks
Kellogg Kel-F 3700	7	Unaffected except for slight discoloration
Kellogg Kel-F 5500-72	7	Unchanged
Du Pont Teflon	7	Unchanged

Table IV. Effect of Immersing Certain Materials in Trimethylaluminum at Elevated Temperature

Material	Temperature, °F.	Time, Hours	Observation
Kellogg Kel-F 5500-72	300–330	1	Reacts
Kellogg Kel F NW-5	250–300	2	Sample dissolved
Kellogg Kel-F 5NW-25TR	240–305	1.5	Sample became porous
Kellogg Kel-F N-1	240–300	1.5	Sample dissolved
Kellogg Kel-F compression-molded film	300	1.5	Reacts
Du Pont extruded black Teflon	350	1.5	Sample recovered unchanged
Du Pont Teflon sheet	350	1.5	Sample recovered unchanged
Du Pont Teflon sheet	400	1.5	Sample recovered unchanged
Du Pont Teflon sheet	450	1.5	Sample recovered unchanged

compounds such as ethers, tertiary amines, and sulfides. In addition, the fillers or plasticizers could also react. The only materials which are compatible with trimethylaluminum at room temperature are polyethylene, Kel-F, and Teflon.

Because of its relatively low softening point, polyethylene cannot be used in any applications at even moderate temperatures. A number of Kel-F elastomers, compression-molded Kel-F film, extruded Teflon, and Teflon sheet were subjected to immersion tests at elevated temperatures. All of the Kel-F materials reacted to some extent. This may be due to the reaction of the trimethylaluminum with the chlorine atoms in the Kel-F polymer, or to the decomposition of the Kel-F by the loss of chlorine and subsequent reaction with the trimethylaluminum.

Ignition Properties of Aluminum Alkyls

There are numerous unclassified literature references to reaction systems containing oxygen and organometallic compounds, but very few of these deal directly with ignition. For example, Bamford and Newett (*3*) have investigated the kinetics and mechanism of oxidation of dimethylzinc and diethylzinc, trimethylantimony and triethylantimony, trimethylboron and tripropylboron, and others. There are also many investigations of the effect of these compounds on the ignition and combustion characteristics of hydrocarbon fuels. The great bulk of these deal with lead alkyls; however, reference to other alkyls and hydrides occasionally appears. For example, Kurz has recently published a paper on the influence of diborane on flame speeds of propane-air mixtures (*6*).

Ignition limits for diborane-oxygen (*9*) and explosion limits for dimethylzinc (*1*) and triethylborane (*4*) have also appeared, but these papers are mostly concerned with kinetics and lack data such as ignition delay values at varying conditions of temperature and pressure.

In conjunction with the synthesis program, previously described, the ignition properties of some organometallic compounds have been investigated, and a limited amount of data is available concerning the spontaneous ignition in air of a series of organoaluminum compounds.

Spontaneous ignition temperatures and ignition delays are not absolute properties, but are strongly dependent upon the system in which they are obtained. Mullin (*7*) has listed several methods in considerable detail; a summary of some of the principal methods is given below.

Drop Methods. Ignition temperature is taken as the lowest temperature of an air-filled cavity which yields ignition when drops of liquid fuel are introduced into it; time intervals are measured, when possible. The following types of apparatus have been used to form the cavity:

1. A covered crucible in a heated metal block, into which air is continuously streamed at the block temperature (Moore).
2. A conical cavity is cut directly into a block replacing the crucible in No. 1; the test is otherwise similar to Moore (Krupp).
3. ASTM method D 286-30 uses a borosilicate glass, conical flask in a gas-heated solder bath; otherwise, it is similar to Moore.
4. A four-compartment test section method in each of which tests are conducted at various oxygen rates, to determine the effect of varying flow rates of gas on ignition temperature. This test defines an ignition value:

$$Z = \frac{T}{b+1}$$

where T = ignition temperature
b = a function of flow rate, bubbles per minute

Z is relatively constant over a wide range of values for b (Jenzsch).

5. A heated enclosure, gas-tight, in which the effect of pressure may be determined.

Despite much controversy regarding the exact meaning and usefulness of these tests, they are still widely used. The principal objections raised concern the lack of control of or difficulty in quantitatively determining the variables involved (such as fuel temperature, fuel to air ratio, ignition delay, etc.).

Flow Methods. These methods generally employ a heated tube through which the combustible mixture passes. Because better mixing of fuel and air is obtained than with the static method, this test often gives results which better approximate those prevailing in the actual use of the fuel.

Adiabatic Compression. This method employs rapid compression of the gas to give a Diesel type of ignition. Compression may be obtained by piston compression, shock tubes, or by having air which is stored at a sufficiently high pressure rush into a tube of fuel at low pressure.

The principal objections to this method are that the temperature and pressure change continuously and drastically during the course of ignition, so that the measurement of these variables is very difficult.

Heated Surface Method. Heated surfaces of solid objects act as igniters for combustible mixtures. These objects may be wires, rods, particles, spheres, or planes. This method not only introduces a surface variable, but also leaves the temperature of the mixture necessary for ignition, unknown. The values obtained generally are higher than those obtained by the other methods.

With organometallic compounds, the ignition delays are so short that special methods must be employed for their determination. Such a method has been developed at New York University.

Ignition under "Static" Conditions. The static ignition tester (Figure 3) consists of a vertical length of 10-inch I.P.S. pipe, which has a ½-inch steel cover plate

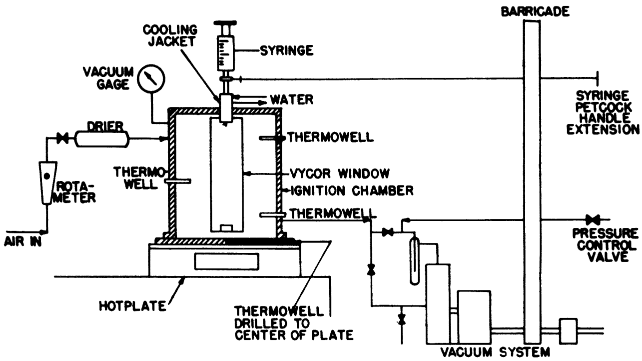


Figure 3. Schematic diagram of static ignition test apparatus

welded to the top. A flanged cover plate, polished on both sides, seals the bottom. Two 2 × 10 inch Vycor windows are mounted vertically at the front and back of the pipe for observation of the interior during testing. Thermowells, air inlet and outlet, and pressure taps enter through the pipe wall. Fuel connections are in the top plate. The entire system when assembled is vacuum-tight. When the vacuum is broken, the bottom cover plate can be dropped off; this makes cleaning the system relatively easy.

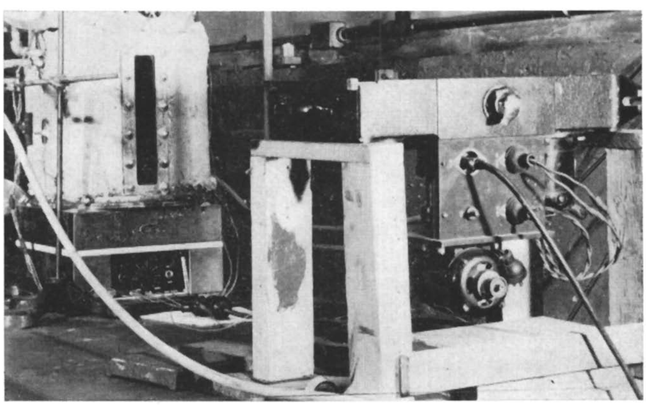


Figure 4. Photograph of static ignition test setup showing test chamber and window

Strobolume and strip camera mounted about 3 feet in front of window

The system is heated at the bottom by a thermostatically controlled hot plate and four strip heaters mounted on the pipe wall. The entire vessel is insulated except at the bottom. Temperatures are taken in the bottom plate and in the bomb interior at three different heights. When working at reduced pressures, vacuum is maintained by pumping against an adjustable leak rate of dry air into the chamber.

In the original system, fuel was introduced from a hypodermic syringe which was closed at the bottom with a syringe stopcock. The hypodermic needle was water-cooled and extended into the test chamber through the top.

A Strobolume light source mounted in the rear provided intense lighting at 1/48-

second intervals. Ignition data were obtained photographically. One of two types of cameras was used:

1. A strip camera (General Radio Corp.) in which there is no frame maker. The film strip moves continuously past an image of the windows. A point of light in the image appears as a horizontal line on the film. A point moving vertically appears as an inclined line and a line or plane of light in the window appears as a band on the film. In addition, every 1/48 second the Strobolume lights the back window. In this way, the first moment of fuel injection is known to 1/48 second. Ignition and propagation of the flame show up as broad bands of light.

2. A Fastax, frame making, high speed motion picture camera. The Strobolume is used here as a timing light only. Backlighting is continuous. The ignition delay is calculated by counting the frames from initial fuel injection to ignition.

Figure 5 shows two strips of a Fastax film record of the ignition of trimethyl-

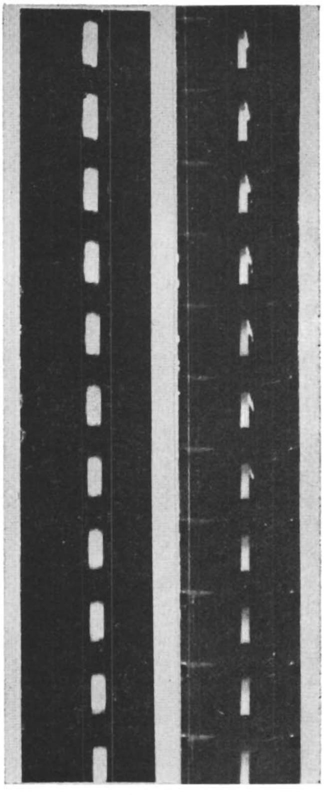


Figure 5. Fastax record of ignition of trimethylaluminum

Conditions. 5 inches of mercury absolute air pressure and 450° F. Ignition shows in left strip, fourth frame down, 26 frames (0.013 second) after start of fuel injection. Second strip shows bomb 0.015 second after ignition

aluminum at room temperature sprayed into air at 450° F. and 5 inches of mercury absolute. The film speed here is about 2000 frames per second. Ignition starts in the fourth frame down, which is 26 frames after the start of injection. This corresponds

to an ignition delay of 13 milliseconds (0.013 second). The right-hand film strip shows the bomb window 15 milliseconds after ignition starts; it can be seen that the flame fills the entire test chamber.

Figure 6 shows film records taken with the strip camera. In all photographs, the

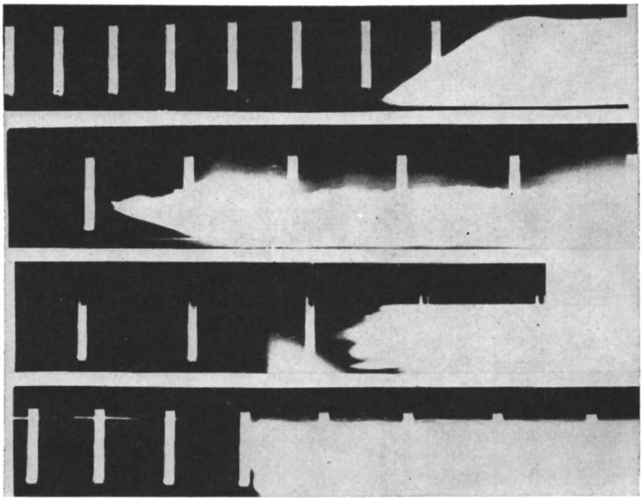


Figure 6. Strip camera records of ignition of various organometallic compounds

A. Tripropylboron
B. Triethylboron without water-cooled needle
C. Triethylboron with water-cooled needle
D. Trimethylaluminum

ignition shows as white streaks. Images of the window appear every 1/48 second as white rectangles; spacing differences are due to different film speeds. Figure 6, *A,* shows the ignition of tripropylboron; *B,* triethylboron; *C,* triethylboron from a water-cooled needle; *D,* trimethylaluminum.

Ignition in Figure 6, *A,* shows bottom firing and movement of the flame up towards the injector needle. Droplets of fuel can be seen entering the chamber from the top. *B* shows no droplets, because the triethylboron flashes off as it enters. *C* with a water-cooled needle shows the droplets. *D* shows ignition starting at the top almost immediately (less than 1/48 second) after fuel injection.

By using these test methods, the ignition delays for several organometallic compounds have been determined (Table V).

Table V. Ignition Delay Values of Selected Compounds at 450° F. and 5 Inches of Mercury Absolute Air Pressure

Compound	Ignition Delay, Second
Dimethylaluminum chloride	0.020
Trimethylaluminum	0.013
Triethylaluminum	0.040
Diethylaluminum bromide	0.150
Diethylzinc	Smoke after 0.040
Triethylborane	0.020
Triisobutylaluminum	Smoking only

A series of static ignition tests was run to determine the effect of pressure and temperature on the ignition characteristics of trimethylaluminum. In this series of experiments it was desirable to have the fuel injected under a constant pressure differential. This was accomplished by replacing the syringe injection system with a

pressurized feed chamber; the pressure difference across a 1/16-inch capillary tube was kept at 30 inches of mercury throughout the series of experiments. The results of this series of runs are summarized in Table VI.

Table VI. Effects of Temperature and Pressure on Ignition of Trimethylaluminum

Chamber Temp. Range, °F.	Absolute Pressure, Inches Hg	Ignition Delay, Msec.
455–60	2	21
450–60	5	13
445–60	30	3
350–65	5	15

A 100° change in air temperature does not appreciably change the ignition delay value. However, the ignition delay decreases considerably as the pressure is increased, and this is to be expected, because the concentration of oxygen and the heating capacity of the air through which the spray travels are increased.

Acknowledgment

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Aluminum Alcoholates and the Commercial Preparation and Uses of Aluminum Isopropylate

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The alkoxides of alcoholates in which metals, such as aluminum, replace the hydrogen of the alcohol group have been known for years. Some of these products are now available commercially and present a challenging field of research in preparing a host of new compounds. Using these compounds, a method of introducing higher, less reactive alcohols into combination with aluminum to form the higher alkoxides is now available; thus the trisoaps of aluminum can now be synthesized. By proper combination of reactants it is possible to prepare aluminum soaps containing three different acid radicals. An extensive literature on the preparation of aluminum alkoxides was available before the turn of the century and the methods then discovered are still in common use not only in the laboratory, but also in commercial operations.

The reaction of alcohols on pure aluminum metal is negligible even at the boiling point of the alcohols. To initiate the reaction a number of reagents have been used and are usually referred to as catalysts. Gladstone and Tribe (*7*) used small amounts of iodine. Wislicenus and Kaufmann (*27*) introduced the amalgamation process. Hillyer and Crooker (*11*) used aluminum chloride and the chlorides of tin. Carbon tetrachloride has also been suggested. A process lately patented in France (*3*) passes alcohol vapor together with an inert gas countercurrent through a heated mixture of copper aluminum alloy and copper chloride. The British have patented a process (*6*) in which aluminum chloride is dissolved in the desired alcohol; anhydrous ammonia or one of the simpler primary amines is then added. The ammonium chloride which precipitates out is filtered off, leaving an alcoholic solution of the desired compound. This reaction is also useful in making iron alcoholates. Meerwein (*25*) found that the alkoxides unite with alcohols to form alkoxy acids which are relatively strong and can be titrated with indicators.

The reaction mechanism is postulated in the equation:

$$Al(OR)_3 + ROH \rightarrow [H^+Al(OR)_4]^-$$

That such a compound is actually present in the alcohol solutions is indicated by the fact that aluminum metal dissolves readily in these solutions much as the metal dissolves in the standard acids.

Laboratory Preparation

On the laboratory scale, aluminum compounds of the lower molecular weight alcohols are readily prepared by using the amalgamation process. The amalgamation is accomplished by placing aluminum turnings in a 2% solution of mercuric chloride. After amalgamation is completed the metal is washed and dried. Alternately, the mercuric chloride is added as a solid to the reaction flask containing the metal and alcohol. All material should be free of water and during reaction the apparatus should include a drying tube containing calcium chloride to protect the reaction mixture. The amalgamated aluminum dissolves readily in the alcohol at reflux temperature. After dissolving all of the metal the excess of alcohol is distilled off and the aluminum alcoholate is then purified by distillation under reduced pressure.

Some difficulty is encountered in purifying the alcoholates in which mercury has been used as a catalyst, because at the temperature of distillation the mercury, which at this stage is present as metal, has an appreciable vapor pressure and distills over, causing the product to be dark. In many cases the impure product is used directly without distilling.

Why did the chemical industry choose aluminum isopropylate as the compound for commercial production? The compounds based on secondary alcohols are more versatile reagents than those based on primary alcohols and isopropyl is the first member of the secondary series. As a raw material, isopropyl alcohol is moderate in price, readily available, and relatively nontoxic. Aluminum isopropylate contains a high proportion of metal, is stable, readily purified, and easily handled in standard containers. There is some demand for a liquid product which would be more convenient in some operations and, if purity is not very important, a product based on mixed alcohols is available (*17*). Starting with aluminum isopropylate it is possible to convert it to the other alcoholates by the ester interchange method of Baker (*2*).

The history of chemistry includes many examples of products which laid on the shelf for years. DDT is a case in point and is familiar to all. The aluminum alcoholates have traveled a similar slow and tortuous course.

. From their first preparation to 1900 most of the effort was expended in making compounds by differing methods and applying them to the reactions known for the alkali metal alcoholates. In 1922, Adkins (*1*) reasoned that aluminum oxide catalysts could be made with varying structure and porosity by decomposing the aluminum alcoholates. He made a series of compounds and noted their properties. Three years later the work of Verley (*24*) and of Meerwein and Schmidt (*16*) led to the discovery that aldehydes could be reduced to alcohols by treatment with aluminum ethoxide in the presence of ethyl alcohol. In 1926 Ponndorf (*20*) showed that the aluminum derivatives of the secondary alcohols made the reactions more general and applied equally well to the reduction of ketones.

The Meerwein–Ponndorf–Verley reduction, as it came to be commonly known, proved a useful tool in the preparation of a number of compounds during the next decade. By using aluminum isopropylate and isopropyl alcohol even the unsaturated aldehydes and ketones were successfully reduced. The reaction is mild, specific, and in most cases produces the desired product in high yield. At the same time the operation is relatively simple. The aldehyde or ketone is mixed with an excess of isopropyl alcohol and aluminum isopropylate and heated. The acetone resulting from the reaction is distilled off as it is formed and side reactions are at a minimum. Even during these early experiments the reversibility of the reaction was realized, but it remained for Oppenauer (*18*) to work out the conditions whereby oxidation could be accomplished. The Oppenauer oxidation depends on the use of an excess of acetone or other ketone in the presence of aluminum alcoholate and has proved extremely useful in steroid chemistry.

All of these findings were extremely important and interesting but during the nearly 60 years in which these events were taking place there was no progress beyond

the test tube stage. It was still a matter of preparing alcoholates as required, in small quantities and commercial availability was still in the future. The impetus for commercial production came from the uses developed in the last 10 to 12 years.

Aluminum isopropylate is analogous to aluminum hydroxide in which the hydrogen atoms have been replaced by isopropyl groups. Using this simple comparison many of the reactions of the alcoholates become obvious. The reaction of aluminum isopropylate with acids to form salts and isopropyl alcohol is comparable to the reaction of aluminum hydroxide with acids to form salts and water. However, because of the trivalency of aluminum and its weakness as a base its reaction with the long-chain fatty acids offers some interesting new possibilities. Until recently there was some doubt as to the existence of the aluminum trisoaps in which all of the aluminum valencies were taken up by fatty acids. When these soaps are prepared by precipitation only mono- or disoaps are produced.

Using aluminum isopropylate it is now possible to make not only the mono- and disoaps, but also the trisoaps. Rinse (*21*) found that treating aluminum alcoholates with fatty acids under carefully controlled conditions results in the formation of trisoaps. The reaction proceeds stepwise and the first two alcohol groups are easily replaced. The third alcohol group is more difficult to replace, since the reaction appears to be reversible. At the same time the alcohol resulting from the reaction is available for the formation of esters which contaminate the product. The equation for the replacement of the first two alcohol groups illustrates the point.

$$Al(OR)_3 + 2R^1COOH \rightarrow AlOR(OOCR^1)_2 + 2ROH$$

If now just enough acid is added to make the trisoap, the two moles of alcohol formed tend to reverse the reaction and to form esters. It is therefore necessary to remove the alcohol as it is formed by operating at elevated temperatures.

The aluminum tritallate as prepared by Rinse (*21*) has several interesting properties which he lists as follows:

Excellent solubility in hydrocarbons, mineral, vegetable, and animal oils to form solutions of low viscosity.

Compatibility with fatty acids, resins, and ester gums.

Rapid partial hydrolysis in presence of water or humid air to solid products with good water resistance.

Reactivity with hydroxy compounds such as glycerol, alcohols, and the phenols.

Using aluminum isopropylate it is possible to make the mono- and disoaps without the contamination of sodium salts encountered in the regular precipitation process. It also is possible to make mixed soaps in which more than one fatty acid is combined to the same aluminum atom. One area where this may be of particular interest is in the preparation of jellied gasolines. A patent (*10*) has already been issued for a liquid composition based on aluminum isopropylate. This liquid compound makes it possible to prepare jellied gasoline in the field as needed, without the use of heat. The field of greases based on aluminum soaps offers an excellent domain for these purer products based on isopropylate.

Aluminum isopropylate is of value to the paint formulator. An extensive literature is accumulating and only a few examples will be used to indicate the areas of interest. Rinse (*21*) finds that the alcoholates increase the viscosity of paints and thus decrease pigment settling. At the same time the product has improved water resistance. A heat-resistant aluminum paint uses aluminum isopropylate as a binder (*5*). When linseed oil is treated with the alcoholates the films dry faster and harder, absorb less oxygen, and have better resistance to water and chemical attack (*22*). Special resins (*9*) are prepared by reacting with glycols and fatty acids. Aluminum isopropylate is a good interesterification catalyst and may be of considerable interest in modifying resins.

Aluminum isopropylate reacts readily with water or water vapor, the end products

being aluminum hydroxide and isopropyl alcohol. Because of its sensitivity to water, the compound should be stored in sealed containers. The reaction with water is an excellent method of preparing pure alumina, because the alcohol is completely removed by application of heat. Pure alumina with a varying pore size was the goal of Adkins back in 1922. Interest in making special grades of alumina has been revived in the last few years. A process for making eta-alumina (*4*) is based on the controlled hydrolysis of higher aluminum alcoholates. The higher alcohols are utilized, because of their water insolubility and the ease of recovery of the alcohol. Vaporized aluminum isopropylate mixed with combustible gases such as hydrogen can be burned to form a finely divided pure alumina. This material is suitable for rubber compounding and as a carrier for phosphorescent and luminescent pigments.

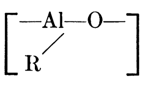
It is known that alcohols, aldehydes, ketones, and esters are basic components in the blending of perfumes. The perfumers were one of the early groups to take advantage of the various organic reactions based on aluminum isopropylate. The Tischenko, Meerwein–Ponndorf–Verley, and Oppenauer reactions are all important methods used in the manufacture and rearrangement of these exotic products.

The use of aluminum isopropylate in steroid chemistry is extremely important to the medical profession and centers around the interconversions of alcohols and ketones by the various reactions mentioned. Production in this field is small and the steroid chemicals represent only a minor consumption of alcoholate. Aluminum isopropylate is also used in the manufacture of vitamin A alcohol, and chloromycetin (*13*).

Antiacids may not come under the strict heading of legitimate drugs, but aluminum isopropylate has found a growing outlet in the manufacture of these products. When aluminum isopropylate reacts with a strong hot water solution of glycine a dihydroxy aluminum glycinate results (*12*), which has excellent antiacid properties. In this compound the two hydroxy groups react readily with acids and the glycine part of the molecule can also act as an acid acceptor. Glycine is one of the amino acids which form zwitterions. A zwitterion is one of those materials which has found out how to make both ends meet. Compounds of other amino acids have been found effective as antiacids (*14*).

Aluminum isopropylate can enter indirectly into the preparation of antiperspirants. When aluminum dihydroxy aminoacetate is reacted with hydrochloric acid a dichloro aluminum aminoacetate results (*8*). This material combines the astringent properties of aluminum chloride with the buffering action of the amino acid.

Work in the area of replacement of the alcohol groups with fatty acids has resulted in the formation of polymeric organic aluminum oxides (*23*). The process consists of treating aluminum isopropylate with less than the theoretical quantity of fatty acid, removing the alcohol and esters which are formed, and then heat treating the product under vacuum to form polymers containing the group



These polymers have surface active properties and are suggested as dispersing agents for pigments, lubricating oil additives, and cross-linking agents for polymers.

Aluminum isopropylate has been proposed for a number of other uses which may be of interest. Williams and Hiatt (*26*) add 6% of the isopropylate to cellulose esters to stabilize their color and viscosity. Orthner and Reuter (*19*) treat fabrics with a solution of aluminum alcoholate and oleic acid in trichloroethylene to reduce the water uptake of the fabrics. Mailander (*15*) uses aluminum isopropylate with octylene glycol and petroleum wax to make fabrics water repellent.

On a commercial scale aluminum isopropylate is made in batches of 1 to 5 tons. Some manufacturers still use a modified amalgamation process where mercuric chloride is added directly to the reactants. Because the added mercury presents some difficulties in the purification step and the process of using aluminum isopropylate as the

catalyst proceeds almost as rapidly, it is just a matter of time before the amalgamation process is supplanted. The aluminum alcoholates when dissolved in alcohols form strong acids which are the explanation for the rapid reaction.

In making aluminum isopropylate in the laboratory or on a small scale all of the aluminum can be added at once. On a commercial scale this is not possible because the reaction gets out of hand. The reaction rate is therefore controlled by adding the metal in 50- to 100-pound increments. After each addition the metal is allowed to react until the evolution of hydrogen subsides, when another increment of metal is added. During the entire operation the alcohol is maintained at the boiling point and provision is made for refluxing the vapor back to the reaction tank. When all of the metal has been added, the refluxing is continued for 3 hours to ensure complete reaction. Since hydrogen is evolved during the reaction, means must be provided to vent the gas and at the same time to avoid forming explosive mixtures with air. The method used is to purge the reactor with an inert gas and to feed the metal through a double valving system. Excess gas is bled from the top of the condenser.

After the aluminum is completely dissolved and the batch has been refluxed, the excess of alcohol is distilled off. The molten aluminum isopropylate is then distilled at reduced pressure and is packed in air-tight steel drums.

Aluminum isopropylate is a white, brittle, solid compound melting at 118°C. and boiling under reduced pressure at 125° to 130°C. at 4 mm. The compound decomposes on exposure to moisture, forming aluminum hydroxide and isopropyl alcohol. Upon heating it is not readily decomposed until about 900°C. It is soluble in isopropyl alcohol, benzene, and mineral spirits. The commercial aluminum isopropylate has a typical analysis of:

Al	13.10%
Aluminum isopropylate	99.40%
Residue	0.5%

One of the problems encountered in the use of aluminum isopropylate is the fact that the material is received as a solid cake in drums. As the melting point is rather high, difficulty is encountered in melting the product in the drum. This hardship can be circumvented by breaking the solid in the drum prior to opening, which is readily accomplished by striking the side of the drum with a hammer or other tool. The isopropylate is very brittle and only a minimum of effort is necessary to break the solid cake so that it can be readily removed.

Of the half million or more chemical compounds which have been synthesized by chemists, only about 5000 products are commercially available and aluminum isopropylate is among them. Its use in paint, plastics, greases, cosmetics, catalysts, drugs, oils, and perfumes suggests that this is a chemical we can be proud of. It not only helps in lubricating the wheels, but it also helps to make us look better, feel better, and even smell better.

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Applications of Organotin Compounds

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Organotin compounds were first studied in 1852 by Löwig (*9*), who prepared diethyltin by the action of a sodium-tin alloy upon ethyl iodide. In the following year Frankland (*4*) prepared tetraethyltin and in the next years a considerable number of both alkyl and aryl organotin compounds were synthesized and described. In the course of these studies more than one of the investigators became aware of the poisonous nature of some of these compounds and Frankland himself was made ill for several months, but happily recovered, and there are no reports that any of those affected actually succumbed. It was evident that certain organotin compounds, notably triethyltin hydroxide and triethyltin acetate, were highly toxic; this was confirmed in 1881 by White (*22*), who studied their effects upon dogs and other animals. A period of 70 years was to elapse before the significance of these preliminary observations was realized.

In 1932 (*13*) a patent was taken out for the use of the tetraalkyltin compounds as stabilizers of chlorinated transformer oils. In 1940 and 1941 patents were taken out by Yngve (*24*) covering the use of various organotin compounds as stabilizers for poly(vinyl chloride). Dibutyltin dilaurate and other dibutyltin salts have since become widely used as stabilizers. The availability of dibutyltin dilaurate as a commercial material may have been a predisposing influence in the selection of this compound for experiments on the treatment of worms in chickens, for which it is now widely used. Methyltin triiodide was marketed in England over 20 years ago as a treatment for boils, but failed to gain wide acceptance. It has been known for centuries that even the rather insoluble dioxide, and the metal itself in powder form, often effected remarkable cures of worm infections both in human beings and in animals, and that tin and its salts had often given positive results in the treatment of staphylococcal infections such as boils. In view of the erratic results with the inorganic forms of tin, it seemed likely that the organotin compounds would be more potent.

Modern Researches

Linking of the tin atom directly to at least one carbon atom is adopted here as the criterion of an organotin compound. As tin, like carbon, is quadrivalent and as preparative chemistry has shown that tin atoms can be linked together in short chains, a considerable field of organic chemistry is possible in which one or more atoms of carbon are replaced by tin atoms. This concept differs somewhat from that of general organometallic chemistry, in view of chemical similarities between tin and carbon.

The International Tin Research Council decided that the time was ripe for the systematic investigation of this new field of organotin chemistry. It was expected that among the vast number of possible new compounds a number would fill some industrial need, but it was necessary to develop methods of synthesis and to study

reaction mechanisms and structural problems. In this field it is easy to be led astray by the ordinary rules of organic chemistry.

The council was fortunate in enlisting, 7 years ago, the enthusiastic collaboration of van der Kerk, director of the Institute for Organic Chemistry, T.N.O., Utrecht, who with a team of assistants has been in charge of the main program of research ever since. His personal contribution to the success of the work is enormous. The council has also, during the past 7 years, sponsored research on different aspects of organotin chemistry in the University of Toulouse in France and in the Universities of London and Southampton in England. In recent years interest in organotin chemistry has spread considerably and the council collaborates with the research departments of universities and technical institutes and with manufacturers and users of organotin compounds in many countries.

Four Main Types of Organotin Compound

The four types of compound may be characterized according to the number of carbon atoms directly linked to tin:

Tetraalkyltin	R_4Sn
Trialkyltin	R_3SnX
Dialkyltin	R_2SnX_2
Monoalkyltin	$RSnX_3$

where R is an alkyl radical and X is any radical not linked through a carbon atom. Corresponding series of aryl compounds exist.

Tetraalkyltin. The tetraalkyltin compounds, such as tetramethyltin and tetraethyltin, are akin to hydrocarbons, but less volatile; volatility decreases as the aggregate of carbon attachments increases through the series. While it is easiest to prepare symmetrical tetraalkyltins in which all the alkyl groups are of identical kind, it is now also possible to prepare them with one, two, three, or all the groups differing:

$$R'_4Sn, \quad R''R'_3Sn, \quad R'''R''R'_2Sn, \quad R''''R'''R''R'Sn$$

The lower tin tetraalkyls—e.g., tetraethyltin—are colorless mobile liquids, with a weak odor when pure. They are insoluble in water but soluble in organic solvents, especially in hydrocarbons, chlorinated hydrocarbons, and ethers. The higher members—tetra-*n*-dodecyltin, etc.—are solids with low melting points. Tin tetraaryls are solids with melting points above 200°C. The lower tin tetraalkyls can be distilled under atmospheric pressure without decomposition. All the compounds are stable in the presence of air and water.

Trialkyltin. The trialkyltin compounds are formed from the tetraalkyl compounds by treatment with a halogen:

$$R_4Sn + X_2 \rightarrow R_3SnX + RX$$

The trialkyltin chlorides, bromides, and iodides are colorless liquids or solids with low melting points showing the same thermal stability as tin tetraalkyls. They are somewhat soluble in water and miscible with organic solvents. The ethyl compounds in particular possess a penetrating and lachrymatory smell. The fluorides are solids with high melting points. All the trialkyltin halides are solids. On shaking the halides with caustic potash solution the hydroxides are formed. These are solids.

Dialkyl- and Diaryltin. The dialkyltin and diaryltin compounds are formed by reaction of the tetraalkyltin with two halogens:

$$R_4Sn + 2X_2 \rightarrow R_2SnX_2 + 2RX$$

The dihalides are crystalline substances which are rather more soluble in water than the monohalides. With dilute alkali they hydrolyze, forming the oxides, R_2SnO. These are white amorphous infusible powders with weakly basic properties. With

strong acids they form normal salts which are stable in water. With weak acids the normal salts can be prepared under special conditions. The dialkyltin and diaryltin salts are much less toxic than the corresponding trialkyl or aryltin salts; some are nontoxic.

The monoalkyl and aryltin compounds in some respects resemble the inorganic tin tetrahalides. The trihydroxides are unknown because the hydrolysis of the halides produces either alkyl or arylstannonic acids, $RSnO_2H$. The stannonic acids are white, amorphous, infusible and insoluble powders, forming salts with both strong acids and bases.

The Distannanes

Another type of compound is the hexaalkyl or hexaaryl distannane, prepared from the corresponding trialkyl or aryltin halides by reduction with sodium.

$$2R_3SnX + 2Na \rightarrow R_6Sn_2 + 2NaX$$

The hexaalkyl distannanes are colorless liquids boiling at from 50° to 100°C. higher than the corresponding tin tetraalkyls. The hexaaryl distannanes are crystalline solids.

Applications and Properties of Organotin Compounds

Table I. Survey of Known Alkyltin Trihalides and Methods Used in Their Preparation (*5*)

Compound	Method of Preparation	Yield, %	Melting Point, °C.	Boiling Point °C.	Boiling Point Mm.
CH_3SnCl_3	CH_3SnOOH + dry HCl at 50°C.		(53), 46		
	$CH_3(C_6H_5)_3Sn + 3SnCl_4$	65	45–46		
CH_3SnBr_3	CH_3SnOOH + fuming HBr	53	53		
	Sn + 1½CH_2Br_2 50 hr. at 180°–220°C.	90	53	210–211	746
CH_3SnI_3	CH_3SnOOH + aq. HI	65	86.5		
	$SnI_2 + 2CH_3I$ 4 hr. at 160°C.	50	85		
	$SnI_4 + 4CH_3MgI$	15	85		
	$KSnCl_3 + CH_3I$ 48 hr. at 90°C.	43.7	85		
$C_2H_5SnCl_3$	$(C_2H_5)_4Sn + 9SnCl_4$ 24 hr. reflux.	15		196–198	760
$C_2H_5SnI_3$	$KSnCl_3 + C_2H_5I$ 48 hr. at 110°C.	37		181–184.5	19
$C_3H_7SnI_3$	$KSnCl_3 + C_3H_7I$ at 130°C.	<25		200 (decomp.)	16
Iso-$C_3H_7SnCl_3$	$KSnCl_3$ + Iso-C_3H_7I at 110°C.	>40		75	16
Iso-$C_3H_7SnBr_3$	Iso-C_3H_7SnOOH + concd. aq. HBr		112		
C_4HiSnI_3	$KSnCl_3$ + C4HiI 72 hr. at 90°C.	25		154	5

The Monoalkyltin Compounds. The only one of the compounds listed in Table I, which has so far had practical application, is methyltin triiodide, which has been tried in medicine as a cure for boils, but not widely acclaimed for this purpose. Further research upon this and other monoalkyl or aryltin trihalides is essential before they can be safely recommended for any pharmacological purpose. Further investigations upon monoalkyltin compounds will doubtless bring to light useful applications, so at this stage they should not be disregarded.

Dialkyltin and Diaryltin Compounds. Plastics Stabilizers. At present the plastics industry consumes the largest tonnage of organotin compounds. This is due to the outstanding ability of the dibutyltin salts to stabilize poly(vinyl chloride). In 1942, Yngve (*25*) specified the use of dibutyltin dilaurate as a vinyl stabilizer. Shortly afterwards, Quattlebaum and Noffsinger (*16*) discovered that dibutyltin maleate was more effective for high temperature processing of the poly(vinyl chloride) because of its double bond, which enables it to react with the colored polyenes forming in heat-degraded vinyl polymer and so to maintain the water-clear color of the resin. In recent years there have been many variations made in the acid radicals—

for example, dibutyltin dithioglycollate has been found even more effective. Synergistic effects result from the use of combinations of the various dibutyltin salts. Mack and Parker (*14*) describe the use of organotin sulfonamides of the general formula

$$R_xSn(R'NO_2SR'')_y$$

where R, R′, and R″ are alkyl or aryl radicals and $x + y = 4$. These substances are plasticizers as well as stabilizers and in reacting with hydrochloric acid they split off sulfonamides which are compatible with vinyl resins. An example of this compound is dibutyltin dibenzene sulfonamide, $(C_4H_9)_2Sn(HNO_2S \cdot C_6H_5)_2$.

Many variants of these and other dibutyltin compounds have been investigated as stabilizers by Banks and his colleagues at the Research Laboratories of the Metal & Thermit Corp., U.S.A., where large scale manufacturing methods have been developed. In England BX Plastics, Ltd., Pure Chemicals, and Albright and Wilson are all actively interested in this field.

The reviews by Smith (*17, 18*) deal in great detail with the theory and practice of stabilizing poly(vinyl chloride), with special emphasis on the value of the dibutyltin compounds for this purpose.

It is generally acknowledged that the organotin stabilizers are in a class by themselves in their ability to preserve the transparency of poly(vinyl chloride), either when being processed or subsequently when exposed to the deteriorating action of sunlight and heat. While the efficiency of the dibutyltin dithioglycollates is also a matter of general agreement, they suffer from the serious disadvantage that they have a very persistent characteristic and objectionable smell. Much effort is still being expended in the attempt to find an ideal method of combining the dialkyltin radical which will be free from this objection.

The toxicity of the dibutyltin salts has long been the subject of some doubt, and particularly there is anxiety as to whether or not it is permissible to use them in plastics which will come into contact with foodstuffs or with the body. There are two main points: the toxicity of the stabilizer itself and the extent to which it may be leached during the use of the plastic for its normal purposes. The latter is of paramount importance, because if leaching were not possible there could be no risk, even if the stabilizer were toxic. The leachability is variable, depending upon the nature of the plastic and the plasticizers used in it, so it is not possible to avoid the issue of toxicity on the score of nonleachability. The toxicity of dibutyltin compounds is deemed in many countries to be sufficiently high to warrant the denial of their use in certain poly(vinyl chloride) plastics where there may be contact with foods or with the mouth, and these stabilizers are avoided so far as possible in these applications.

Recent experiments carried out in Holland, France, and Germany (*20*) showed that the toxicity of the dialkyltin compounds declines for chain lengths greater than butyl. Experiments by Barnes (*19*) at the Toxicology Unit of the Medical Research Council in England have confirmed that dioctyltin compounds are not toxic when taken by mouth and that very large amounts of them may be ingested by experimental animals without ill effects. No tests have been carried out upon human subjects, but it is unlikely that this is necessary. The way appears to be open now to the use of dioctyltin compounds, which will open entirely new fields of applications to replace dibutyltin salts. The stabilizing action of the dioctyltin salts has been shown to be as good as that of the dibutyltin salts and their compatibility with the plastic is beyond question.

Chlorinated Rubber Stabilizer (5). The stabilizing property of the dialkyltin salts has been shown at the Tin Research Institute to extend to chlorinated rubber and to paints formulated with it. Dibutyltin dilaurate, in amounts equal to only 0.1% of the weight of the chlorinated rubber, is an effective stabilizer for commercial

chlorinated paints. At least one well-known firm in England is manufacturing a tin-stabilized paint.

Anthelmintic Property of Dialkyltin Salts (*6*). Tin and its salts have been used in medicines for the treatment of worm infections in human beings and animals for a century or more. The inorganic tin preparations are safe and they produce no unpleasant effects in the subject, but their curative effect is uncertain. When dibutyltin dilaurate became available industrially about 10 years ago it was thought that tin in this form might be more potent. Trials showed that this was the case with poultry and there has developed a very big outlet for this compound and its analogs as a worm cure and prophylactic for poultry. The material is formulated as a powder, which is added to the bird's daily mash.

Organotin compounds should not be used for the cure of worms in animals or human beings without due care. Fowls may be exceptionally immune to the action of such organotin compounds when taken by mouth (*23*). One preparation of diethyltin diiodide, administered medicinally, is suspected of having been responsible for deaths of human beings in France during 1953 (*19*).

A measure of success has been reported in the treatment of warble fly infestation of cattle (*23*) with dibutyltin dilaurate but further confirmation of its effectiveness is necessary. The possibility of an active impurity in the material has to be examined.

In general, there appears to be a marked diminution in biocidal activity of dialkyltin compounds as the chain lengths increase beyond butyl. For example, dioctyltin dilaurate and other dioctyltin salts have been shown to be nontoxic (*19*). In the case of dioctyltin dilaurate, 400 mg. per kg. of body weight by mouth in arachis oil produced no loss of weight nor any signs of poisoning in rabbits, rats, mice, and guinea pigs. At post-mortem the animals appeared healthy. Applied repeatedly to the skin of rats, a solution of dioctyltin dilaurate in dimethyl phthalate produced no local damage to the skin and no effects of poisoning. Diethyl, dimethyl, dipropyl, and dibutyl dilaurate tested on the skin in the same solvent caused irritation. The dimethyl and diethyl salts produced superficial skin damage only. The dipropyltin, diisopropyltin, and dibutyltin salts produced a deeper seated lesion in the skin and tissues below and all attacked the bile duct. The dipentyltin, dihexyltin, and dioctyltin did not injure the skin or deeper tissues, but the first two caused severe loss of weight and the animals were ill for a reason that was not established.

The dioctyltin dilaurate and dichloride had no demonstrable toxicity when given to four species of animals in repeated doses of moderately large size. It differs very markedly in this respect from the other dialkyltin salts. It seems highly probable that dioctyltin dilaurate and other salts should constitute no health hazard if used as stabilizers in poly(vinyl chloride) plastics.

Antidote. The effects of dimercaprol (BAL) have been studied by Barnes (*11*) on the survival times of rats which had been given 20 mg. per kg. of diethyltin dichloride (intraperitoneally in Tween 80) (Table II).

Table II. Effect of Dimercaprol (BAL) (30 Mg. per Kg. I.M. in Oil) on Survival Time of Rats Given 20 Mg. per Kg. of Diethyltin Dichloride (I.P. in Tween 80)

(Untreated rats were given equivalent volume of arachis oil i.m. Number of rats shown in parentheses)

Treatment	Survival Time			
	Treated, days		Untreated, hr.	
BAL given 30 min. before and 6 hr. after injection of diethyltin	3	(1)	5½	(1)
	7	(2)	<24	(3)
	>7	(1)		
BAL given at 2 and 6 hr. after injection of diethyl, tin	>7	(3)	<24	(3)

Trialkyltin and Triaryltin Compounds. The biocidal action of certain trialkyltin and triaryltin compounds above all others makes them of interest. The following investigations were all carried out by van der Kerk and his team at Utrecht (*11*). The influence of the number of carbon atoms directly attached to the tin atom is well shown in Table III (*11*).

Table III. Influence of Number of Alkyl Groups Directly Attached to Tin Atom on Antifungal Properties of Ethyltin Compounds (*19*)

Compound				Concn. (P.P.M. = Mg./L.) Causing Complete Inhibition of Growth of Fungi			
No.	Name	Formula	Type	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*	*Rhizopus nigricans*
2	Tetraethyltin	$(C_2H_5)_4Sn$	I	50	>1000	100	100
3	Triethyltin chloride	$(C_2H_5)_3SnCl$	II	0.5	2	5	2
23	Diethyltin dichloride	$(C_2H_5)_2SnCl_2$	III	100	100	500	200
24	Ethyltin trichloride	$C_2H_5SnCl_3$	IV	>1000	>1000	>1000	>1000
	Stannic chloride	$SnCl_4$	—	>1000	>1000	>1000	>1000
	Stannous chloride	$SnCl_2 \cdot 2H_2O$	—	>1000	>1000	>1000	>1000

Tetra-, di-, and monoethyltin compounds, as well as the stannous and stannic salts, have little or no fungitoxicity. By contrast, however, the triethyltin chloride is extremely fungitoxic. This is surprising because the fungitoxicity of other metals such as mercury, copper, cadmium, and zinc is not related to the type of organic structure they are combined with and they are fungitoxic whether as organic or inorganic compounds.

Studies of the fungitoxicity of trialkyltin compounds were carried out by systematically varying the attached acidic or alkyl groups.

Table IV. Influence of Varying Group X on Antifungal Properties of Compounds with the General Formula $(C_2H_5)_3SnX$ (*11*)

Compound			Concn. (P.P.M. = Mg./L.) Causing Complete Inhibition of Growth of Fungi			
No.	Name	Formula	*Botrytis allii*	*Penicillum italicum*	*Aspergillus niger*	*Rhizopus nigricans*
8	Triethyltin hydroxide	$(C_2H_5)_3SnOH$	0.2	5	0.5	0.5
3	Triethyltin chloride	$(C_2H_5)_3SnCl$	0.5	2	5	2
19	Triethyltin bromide	$(C_2H_5)_3SnBr$	0.5	2	1	1
22	Triethyltin iodide	$(C_2H_5)_3SnI$	0.5	1	5	2
21	Triethyltin sulfide	$[(C_2H_5)_3Sn]_2S$	0.2	1	1	1
9	Triethyltin sulfate	$[(C_2H_5)_3Sn]_2SO_4$	0.2	0.2	5	5
10	Triethyltin acetate	$(C_2H_5)_3SnO—CO—CH_3$	1	2	5	2
11	Triethyltin caproate	$(C_2H_5)_3SnO—CO—C_5H_{11}$	1	5	2	2
12	Triethyltin laurate	$(C_2H_5)_3SnO—CO—C_{11}H_{23}$	0.2	0.2	5	5
13	Triethyltin benzoate	$(C_2H_5)_3SnO—CO—C_6H_5$	2	10	5	5
15	Triethyltin malonate	$[(C_2H_5)_3SnO—CO—]_2CH_2$	0.5	5	2	1
14	Triethyltin maleate	$[(C_2H_5)_3SnO—CO—CH=]_2$	0.5	5	0.5	0.5
16	Triethyltin phenoxide	$(C_2H_5)_3SnO—C_6H_5$	0.5	1	2	1
17	Triethyltin *p*-nitrophenoxide	$(C_2H_5)_3SnO—C_6H_4—NO_2(p)$	0.5	2	2	2
4	*p*-Triethylstannylsulfonyltoluene	$(C_2H_5)_3Sn—SO_2—C_6H_4—CH_3(p)$	1	5	2	2
5	Triethyltin toluene-*p*-sulfonamide	$(C_2H_5)_3SnNH—SO_2—C_6H_4—CH_3(p)$	1	5	2	5
6	Triethyltin methanesulfonamide	$(C_2H_5)_3SnNH—SO_2—CH_3$	0.5	5	2	2
18	*N*-Triethylstannylsaccharin	$(C_2H_5)_3SnN\langle{}^{CO}_{SO_2}\rangle C_6H_4(o)$	1	10	2	2
7	*N*-Triethylstannylphthalimide	$(C_2H_5)_3SnN\langle{}^{CO}_{CO}\rangle C_6H_4(o)$	0.2	5	1	2

Table IV shows that relatively slight variations occur in the fungitoxicity of triethyl salts of a wide range of inorganic and organic acids.

Varying the three alkyl groups attached to the tin atom, but using always the same salt—the acetate—revealed that the fungitoxicity was linked with the chain length of alkyl groups. The fungitoxicity of symmetrical trialkyltin acetates,

Table V. Influence of Varying Group R on Antifungal Properties of Compounds $R_3SnO—CO—CH_3$ (11)

Compound			Concn. (P.P.M. = Mg./L.) Causing Complete Inhibition of Growth of Fungi			
No.	Name	Formula	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*	*Rhizopus nigricans*
1	Trimethyltin acetate	$(CH_3)_3SnO—CO—CH_3$	20	20	200	200
10	Triethyltin acetate	$(C_2H_5)_3SnO—CO—CH_3$	1	2	5	2
25	Tri-*n*-propyltin acetate	$(C_3H_7)_3SnO—CO—CH_3$	0.1	0.1	1	1
26	Triisopropyltin acetate	$(C_3H_7)_3SnO—CO—CH_3$	0.1	0.1	1	0.5
28	Tri-*n*-butyltin acetate	$(C_4H_9)_3SnO—CO—CH_3$	0.1	0.1	0.5	0.5
29	Tri-*n*-pentyltin acetate	$(C_5H_{11})_3SnO—CO—CH_3$	0.2	5	5	10
30	Tri-*n*-hexyltin acetate	$(C_6H_{13})_3SnO—CO—CH_3$	1	10	20	100
31	Tri-*n*-octyltin acetate	$(C_8H_{17})_3SnO—CO—CH_3$	>100	>100	>100	>100
32	Tricyclohexyltin acetate	$(C_6H_{11})_3SnO—CO—CH_3$	0.5	0.5	5	20
33	Triphenyltin acetate	$(C_6H_5)_3SnO—CO—CH_3$	2	1	0.5	10
49	Phenylmercuric bromide	C_6H_5HgBr	0.1	0.1	0.1	2
50	Phenylmercuric acetate	$C_6H_5HgO—CO—CH_3$	0.5	0.5	0.5	5

in which all three alkyl groups are the same, shows gradation through the series, being low with trimethyl, maximal with tri-*n*-butyl, and declining to almost negligible values in the trioctyls. Tricyclohexyl is about as toxic as tripentyl and the triphenyl is of about the same order of toxicity as triethyl. For comparison, figures for phenylmercuric bromide and acetate are included. Their fungitoxicity is about the same as that of tributyltin acetate.

Another variation is shown in Table VI, in which two of the alkyls are always ethyls and the third ranges from ethyl to dodecyl. The maximal fungitoxicity is possessed by the diethylhexyltin acetate.

Table VI. Antifungal Activity of a Series of Diethylalkyltin Acetates (11)

Compound			Concn. (P.P.M. = Mg./L.) Causing Complete Inhibition of Growth of Fungi			
No.	Name	Formula	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*	*Rhizopus nigricans*
10	Triethyltin acetate	$(C_2H_5)_3SnO—CO—CH_3$	1	2	5	2
41	Diethyl-*n*-butyltin acetate	$(C_2H_5)_2(C_4H_9)SnO—CO—CH_3$	0.1	1	0.5	0.5
42	Diethyl-*n*-hexyltin acetate	$(C_2H_5)_2(C_6H_{13})SnO—CO—CH_3$	0.05	0.5	0.1	0.1
43	Diethyl-*n*-octyltin acetate	$(C_2H_5)_2(C_8H_{17})SnO—CO—CH_3$	0.02	0.5	0.1	>5
44	Diethyl-*n*-dodecyltin acetate	$(C_2H_5)_2(C_{12}H_{25})SnO—CO—CH_3$	0.2	5	0.5	50

For comparison, the fungitoxicity of some unsymmetrical trialkyltin acetates is given in Table VII.

Table VII. Antifungal Activity of Some Further Unsymmetrical Trialkyltin Acetates (11)

Compound			Concn. (P.P.M. = Mg./L.) Causing Complete Inhibition of Growth of Fungi			
No.	Name	Formula	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*	*Rhizopus nigricans*
45	Dimethyl-*n*-butyltin acetate	$(CH_3)_2(C_4H_9)SnO—CO—CH_3$	1	2	5	5
46	Dimethyl-*n*-octyltin acetate	$(CH_3)_2(C_8H_{17})SnO—CO—CH_3$	0.5	0.5	0.2	2
47	Dimethyl-*n*-dodecyltin acetate	$(CH_3)_2(C_{12}H_{25})SnO—CO—CH_3$	0.2	1	0.2	10
48	Ethyldi-*n*-pentyltin acetate	$(C_2H_5)(C_5H_{11})_2SnO—CO—CH_3$	0.2	1	1	0.5

When the sum total of the carbon atoms in the three alkyl chains ranges from 10 to 12, the fungitoxicity is at a maximum.

Some mixed aliphatic-aromatic compounds have been made and also some aromatic compounds containing halogen in the benzene nucleus. The test results are summarized in Table VIII. Introduction of halogen into the phenyl groups does not always have the effect of increasing the fungitoxicity. Diethyl-*p*-chlorophenyltin is somewhat more toxic than diethylphenyltin, but the tris-*p*-chlorophenyltin is of diminished antifungal activity. It is very unusual to find an example of a biocidal compound in which the replacement of phenyl groups by *p*-chlorophenyl groups does not lead to an increase in biocidal activity.

Table VIII. Antifungal Activity of Some Mixed Aliphatic-Aromatic and of Halogen-Substituted Aromatic Tin Compounds (11)

Compound			Concn. (P.P.M. = Mg./L.) Causing Complete Inhibition of Growth of Fungi			
No.	Name	Formula	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*	*Rhizopus nigricans*
36	Diethylphenyltin acetate	$(C_2H_5)_2(C_6H_5)SnO—CO—CH_3$	1	5	2	5
37	Ethyldiphenyltin acetate	$(C_2H_5)(C_6H_5)_2SnO—CO—CH_3$	0.5	1	1	5
38	*n*-Octyldiphenyltin acetate	$(C_8H_{17})(C_6H_5)_2SnO—CO—CH_3$	10	5	5	20
39	Diethyl-*p*-bromophenyltin acetate	$(C_2H_5)_2(BrC_6H_4)SnO—CO—CH_3$	0.2	0.5	1	1
40	Diethyl-*p*-chlorophenyltin acetate	$(C_2H_5)_2(ClC_6H_4)SnO—CO—CH_3$	0.1	1	1	2
34	Tris-*p*-chlorophenyltin acetate	$(ClC_6H_4)_3SnO—CO—CH_3$	20	20	50	>100

Toxicity to Mammals

The toxicity of the organotin compounds has been studied by several investigators. Barnes and his collaborators have published a number of papers dealing with the physiological effects produced by organotin compounds and the lethal doses of a large number of the alkyltins have been determined.

Some of these results are embodied in Table IX (*19*). Triethyltin hydroxide is the most toxic whether administered by injection or by mouth. Intraperitoneal injection of tri-*n*-butyltin acetate shows this material to be nearly as toxic by this route. On the other hand, the oral LD_{50} is considerably greater than for triethyltin hydroxide in the case of the rat. Later work suggests that the LD_{50} for rats for

Table IX. Certainly Lethal Doses (Mg. per Kg. of Body Weight) of a Range of Organic Tin Compounds

Compound	Rabbit Oral	Rabbit I.p.	Rat Oral	Rat I.p.	Guinea-pig Oral
Trimethyl	—	—	30	16	—
Triethyl	10	10	10	10 (LD_{50} 5·7)	5–10
Tri-*n*-propyl	—	—	<40	—	—
Tri-iso-propyl	—	—	80	—	—
Tri-*n*-butyl	60	—	50–100	10	20
Tri-*n*-hexyl	—	—	>100	—	—
Triphenyl	>40	—	>150	—	10
Diethyl phenyl	—	—	50–100	—	—
dichloride	—	—	>40	15	—
diiodide	—	—	100	26	—
Dibutyl dichloride	—	—	100	—	—
dilaurate	—	—	—	85	—
Monoethyl trichloride	—	—	—	200	—

tributyltin acetate given by mouth is nearer 400 mg. per kg. In the case of trioctyltin acetate 400 mg. per kg. was without effect and intraperitoneal injection of 48 mg. per kg. was not fatal. It appears, therefore, that the mammalian toxicity follows the same general course as the fungal toxicity, decreasing as the chain lengths of the alkyls attached to the tin atom increase. There is no evidence in this work that the tin is concentrated in any particular organ but there are usually strong effects on the central nervous system. If the animals do not die at once or within a very few days as a result of the administration of the organotin compound, they make a complete recovery and the organs show no permanent damage.

It is reassuring to note that Luijten and van der Kerk state (*12*):

> Organotin compounds are also toxic towards humans, the first symptoms of poisoning resembling symptoms of concussion of the brain. During our work, carried out for five years with no other precautions than those normal in chemical laboratory practice, only a few isolated cases of sternutatory or vesicant action were noted.

Biocidal Applications of Trialkyltin Compounds

The antifungal properties of the trialkyltin compounds have aroused the greatest interest, because they are clearly of a very high order, comparable with those of organomercurials. There is one obvious advantage possessed by the organotins as compared with other biocidal agents, in that the most acute toxicity is specifically a property of the tin atom only so long as it is joined directly to three carbon atoms, and so soon as even one of these bonds with carbon has been broken there is a great fall in toxicity. By successive breakages of the two remaining carbon bonds the tin is transformed into the normally harmless inorganic tin. There is, therefore, the attractive possibility that when trialkyltin compounds have been used as fungicides, the residues become in the course of time changed into a harmless material.

In view of the general biocidal activity of the trialkyltin compounds (*10*), their use so far has been restricted to applications where there is no risk to animals or human beings. The preservation of wood is a suitable field of application because there is no risk of killing living matter other than the fungus. Similarly, paper, textiles, paints, and other nonliving materials are suitable for treatment. It is a different matter, however, when one considers the contact of trialkyl salts and living matter which must not be killed. For example, phytotoxicity has to be considered.

Although in the discussion of the fungitoxic character of trialkyltin compounds a considerable number of substances were considered, not all of these are commercially available for practical application. One dominating factor is that the dibutyltin salts are being made commercially on a large scale and it is fairly easy to vary the method of manufacture so as to produce tributyltin salts also. This is not the case with any other organotin compound and if others are required they have to be made specially.

However, with an increasing interest in the antifungal and other biocidal qualities of organotin compounds it is anticipated that a number of them may become available commercially.

Wood Preservation

Successful trials have been made in the preservation of various woods against fungi and against wood-boring marine animals (*1*). Trials with different woods have been made in mines in Cornwall and in Cumberland, where the conditions favored rapid destruction of the timber by fungal growth. Exposures of 2 and 3 years have so far fully confirmed the antifungal action of the triethyltin hydroxide which was used to impregnate these timbers. The solution was of 0.5% strength and the timbers were impregnated by being vacuumized while immersed in the hot solution; the tank was then allowed to cool down overnight. This method is not applicable with the tributyl oxide or acetate because of their low solubilities, and solvent impregnation of the timber is necessary if either of these salts is used.

Wood block tests have been carried out in a number of research laboratories with favorable results. The resistance of both triethyltin hydroxide and tributyltin acetate to leaching is particularly good. The value of impregnation with triethyltin or tributyltin compounds appears to be beyond dispute, but the costs, as compared with creosote and other wood preservatives, have not yet been thoroughly determined. Perhaps they may be used in conjunction with other wood preservatives which are more prone to leaching.

An important feature in favor of the organotin compounds is that they impart neither color nor odor to the treated wood. They can, therefore, be used upon light colored woods such as are used for furniture. Wood treated with organotin compounds can be painted normally and there is no risk of subsequent discoloration. The organotin compounds do not increase the risk of fire. It is also possible to apply tributyltin compound in a solvent to joists, floors, and skirtings, etc., in existing structures either by brush or by spray, with a view to preventing the spread of molds and dry rot. It is not yet known whether tributyltin acetate is effective in preventing the attack of the furniture beetle, but a program of tests on this is being carried out in Berlin by Becker. Other tests which are in progress include its resistance to the white ant, but again the work has not yet been completed. Much appears to depend upon the depth of the impregnation obtained and the concentration in the surface layers.

Teredo Tests on Wood. Tests carried out by the Tin Research Institute at Shoreham Harbour in England showed that impregnation with triethyl and tributyl salts was as effective as creosote against the teredo wood-boring worm. The tributyltin acetate also reduced gribble attack to trifling amounts.

Ropes

Some tests were carried out in Shoreham Harbour to ascertain the value of trialkyltin compounds for preserving ropes. As compared with untreated ropes and ropes treated by impregnation with two commercial preservatives, the trialkyltin solutions were very effective. All the ropes which were impregnated with trialkyltin compounds survived the test and were withdrawn without breakage, whereas 13 out of 16 of the other ropes broke either during withdrawal or at the first slight tension put upon them in the laboratory.

Wood Pulp

Trials which have now been going on for over a year at some paper mills in Canada show that a dispersion of triethyltin oxide is a complete preventive of slime

formation during the manufacture of wood pulp. Amounts of less than 1 p.p.m. of the water used are effective in controlling the slime. The effluent water is free from organotin compound in significant amount, and the tributyltin oxide remaining in the paper is too small in amount to be appreciable: During calendering and exposure to heat, light, and air there should be a fairly complete breakdown of the residual tributyltin compound into harmless inorganic tin; this may well prove to be a decisive advantage for the organotin compounds as compared with other slimicides which are in common use at present.

Paints

Excellent results have been reported with small amounts of tributyltin acetate as a fungistat in poly(vinyl acetate) paints (*7, 8*). In tests carried out recently in England in which all the usual fungistatic materials for paints were included, tributyltin hydroxide was effective at a concentration of 1 part in 4000 under very bad conditions in which all the other fungistats were ineffective even at 16 times this concentration. Practical trials in tropical and subtropical atmospheres have confirmed that tributyltin oxide at low concentrations prevents the growth of disfiguring fungi during the whole life of the paint.

Antifouling Compositions

Preliminary laboratory work in England showed that triethyltin hydroxide at high dilution killed the larvae of barnacles and other organisms concerned with marine fouling. This work was followed by several years of testing of painted wooden panels which were immersed in sea water in the Tin Research Institute's raft in Shoreham Harbour. Triethyltin compounds again showed their effectiveness, in that panels treated with a paint containing triethyltin compounds were entirely free from fouling organisms or weed for many months. The safe period was followed by rather sudden breakdown, associated undoubtedly with the high rate of leaching of these compounds.

The rate of leaching of tributyltin compounds in sea water is much less and the tributyltin compounds in fact preserve their antifouling effect for much longer periods. As is well recognized in this field, the whole problem is bound up with compatibility with the particular paint medium. Although no commercially acceptable antifouling composition based on organotin compounds is yet available, the right kind of action is there and practical tests are being continued in collaboration with paint manufacturers.

Textiles

Wool impregnated with tributyltin acetate is immune to attack by moth and by carpet beetle. It is a complete immunity, in that the grubs do not even begin to feed upon the treated samples, so there must be a repellent action. For fabrics which have to be washed frequently it will be necessary to choose an organotin compound with greater resistance to leaching than is possessed by the tributyltin acetate. In cases where the fabrics will come into contact with the skin, it will first be necessary to be satisfied that there is no absorption of the tin compound through the skin.

Jute is often exposed to moist conditions favoring fungal growth which rots the fiber. Tests with buried strips of jute in a tropical climate showed that there was virtually no deterioration of treated jute samples after one month, but the untreated controls lost all their strength in a few days.

Crop Protection (3, *10*)

The unique properties of organotin compounds as biocidal agents make them worthy of very serious study in agriculture, although there are difficulties to be overcome.

On the credit side are the admittedly high fungicidal action and the toxicity to insect pests. For example, the triethyltin and tributyltin compounds are toxic to red spider. The nonpermanent character of the toxicity of the organotin compounds is of great potential interest for two reasons. First, these compounds ultimately decompose under the action of light and air into harmless inorganic tin and there is therefore no danger of the land's becoming poisoned so that crops either cannot grow or, if they do, contain undesirable amounts of toxic substances. Elemental tin appears to be entirely without trace effects upon living matter. Secondly, it may be possible to develop organotin compounds which are toxic to fungi and pests when applied but which decompose into inorganic tin within a few days and leave only harmless residues on the crops when harvested.

On the debit side, the rather crude trialkyltin compounds, which are the only ones so far tested, are toxic to fungi and to pests but are toxic also to the plants which it is their purpose to protect. It is essential that new types of organotin compounds be found which are selectively toxic to the pests and not to the plants. Much work remains to be done here, but the work of van der Kerk and others has already demonstrated that fungitoxicity and phytotoxicity do not always run parallel. Indications have been obtained that highly fungitoxic organotin compounds may possess no higher phytotoxicity than certain organomercury compounds now in common use as seed disinfectants. Moreover, phytotoxicity can be reduced considerably by proper formulation. Perhaps more promising still is the possibility of preparing functionally substituted organotin compounds.

Tetraalkyl- and Aryltin Compounds

Table X (*11*) shows some of the properties of tetraalkyltins, which are of a different order of toxicity from the trialkyls (*21*).

Table X. Melting and Boiling Points of Some Compounds of the Type R_4Sn(*11*)

Name of Compound	Formula	M.P., °C.	B.P. °C.	B.P. Mm.
Methylstannane	CH_3SnH_3		0	760
Dimethylstannane	$(CH_3)_2SnH_2$		35	760
Trimethylstannane	$(CH_3)_3SnH$		59	760
Tetramethyltin	$(CH_3)_4Sn$		78	760
Tetraethyltin	$(C_2H_5)_4Sn$	−112	175	760
Tetra-*n*-propyltin	$(C_3H_7)_4Sn$		222–225	760
			116	13
Tetra-*n*-butyltin	$(C_4H_9)_4Sn$		145	10
Tetra-*n*-dodecyltin	$(C_{12}H_{25})_4Sn$	15–16		

Table XI, based on the work of Meynier (*2, 15*), shows the mammalian toxicity of eight tetraalkyltin compounds towards mice. The first two columns are intraperitoneal doses, the next two columns are intravenous doses, columns 5 and 6 give intramuscular doses, and the last two columns are doses by oral administration. The maximum toxicity is associated with the smallest number of carbon atoms directly attached to the tin. As the chain lengths grow, up to octyl, the biocidal action shows a consistent decline and the tetraoctyl, for example, is markedly less toxic than tetrahexyl or tetraheptyl. No figures are as yet published for mixed tetraalkyltins or tetraaryltins.

Table XI. Toxicity of Tetraalkyltin Compounds to Mice (15)

Alkyl Group	Formula	Maximum Never Fatal Dose, Mmoles/Kg.[a]			
		I.p.[b]	I.v.[c]	I.m.[d]	O.[e]
Methyl	$(CH_3)_4Sn$	0.01	0.4	0.2	0.1
Ethyl	$(C_2H_5)_4Sn$	0.005	0.4	0.1	0.1
n-Propyl	$(C_3H_7)_4Sn$	0.2	0.2	0.1	0.1
Isopropyl	$(C_3H_7)_4Sn$	0.05	0.005	0.1	0.1
n-Butyl	$(C_4H_9)_4Sn$	0.5	0.5	3.0	2.0
Isobutyl	$(C_4H_9)_4Sn$	0.1	0.01	0.2	0.5
n-Amyl	$(C_5H_{11})_4Sn$	0.25	0.25	2.0	1.0
Isoamyl	$(C_5H_{11})_4Sn$	0.05	0.05	0.5	0.25
Hexyl	$(C_6H_{13})_4Sn$	1.0	1.0	2.0	—
Heptyl	$(C_7H_{15})_4Sn$	0.75	2.0	10.0	—
Octyl	$(C_8H_{17})_4Sn$	40.0	<4.0	>20.0	>20.0

[a] Millemoles per kilogram of body weight.
[b] Intraperitoneal.
[c] Intravenous.
[d] Intramuscular.
[e] Oral.

In general, the toxic effects of the tetraalkyltins or tetraaryltins are slower to manifest themselves than the corresponding tri- compounds and in some cases the action may be delayed for 30 days or even longer. When toxic symptoms do appear, they are identical in character to those caused by trialkyltin compounds and this fact suggests that there is first a breakdown of the tetra- compound into the tri- form and that this is the effective toxic agent.

Almost the only use of the tetraalkyltin and tetraaryltin compounds has been as additives to chlorinated hydrocarbons used as coolants for electrical transformers. Amounts of the order of 1% of these tetra- compounds are effective in absorbing the hydrochloric acid which tends to be split off at elevated temperatures and which, if not neutralized, acts as an autocatalyst of further decomposition.

The tetraalkyltins are notably different from the other categories of organotin compounds, in that all their four bonds are linked to carbon atoms in an exactly analogous way to the carbon atom at a tertiary junction in an organic compound:

$$\begin{array}{c} R''' \\ | \\ R''—Sn—R'''' \\ | \\ R' \end{array} \qquad\qquad \begin{array}{c} R''' \\ | \\ R''—C—R'''' \\ | \\ R' \end{array}$$

As hydrocarbons, compounds of this type would not appear to have outstandingly interesting features, but a totally new field of possibilities has been opened up by the discovery of a method by which functional groups can be introduced into one or more of the carbon chains attached to the tin atom. Evidently it is now possible to prepare compounds which are exact analogs of organic compounds of the tertiary type but which have a tin atom instead of a carbon at the branching point. Such organotin compounds as the following have already been made and, in theory, almost any type of functional group can now be introduced into organotin compounds in imitation of carbon compounds, with the limitation only that all such compounds are essentially of the tertiary type. This limitation is due to the fact that if the tin atom carries one or more hydrogen atoms it is, in fact, a hydride and consequently very reactive to any source of oxygen in its vicinity. The possibility of stable compounds based on chains of methylenic-tin units, $—SnH_2—$, in simulation of ordinary methylenic groups, $—CH_2—$, is excluded if reducible substances are present.

To sum up, there now exists the possibility of preparing compounds of the general type:

$$\begin{array}{c} R' \\ | \\ CH_3—(CH_2)_n—Sn—(CH_2)_n—X \\ | \\ R'' \end{array}$$

where X is the functional group, with the proviso that, for stability, R′ and R″ shall be sufficiently large groups, either alkyl or aryl, to screen the tin atom from oxidation.

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Organotin Compounds

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The valences, syntheses and by-product formations, and reactions of organotin compounds are discussed. The general physical properties and physiological effects of these compounds are described. Commercial uses of organotin compounds are given.

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According to the definition of Gilman, an organometallic compound must contain a carbon to metal bond. This paper will discuss only those compounds containing a carbon to tin bond. Tin can exhibit covalences of two and four (*38*), as well as complex valences of six (*15*). Inorganic tin compounds showing all these valences are common: The stannous or bivalent form is represented by the stannous salts, the stannic or quadrivalent by tin tetrachloride and similar compounds, and the sexivalent by the metal stannates such as sodium stannate. Although organotin compounds of all these valences are known, only the quadrivalent ones are common.

In addition to the multiple valences, tin may be substituted successively with one to four organic groups, while the remainder of the valences are filled by electronegative groups. The possible structures are $(R_2Sn)_y$, $R_3Sn—SnR_3$, $RSnX_3$, R_2SnX_2, R_3SnX, R_4Sn, and $M[SnR_nX_{6-n}]$. Using R = butyl, $(R_2Sn)_y$ represents dibutyltin which is known only in polymeric form; $R_3Sn—SnR_3$ is hexabutylditin; $RSnX_3$, butyltin trichloride; R_2SnX_2, dibutyltin dichloride; R_3SnX, tributyltin chloride; and R_4Sn, tetrabutyltin. The $M_2[SnR_nS_{6-n}]$ structure is not known in any simple form but only in the complexes of Harada (*14*) and in some recent industrial compounds. Both the disubstituted tins and the hexasubstituted ditins are very susceptible to oxidation. They have no commercial value and are actually troublesome as by-products in the synthesis of quadrivalent compounds.

Preparation

Although many synthetic processes are known for the preparation of organotin compounds, only three are feasible for commercial production.

Wurtz. Alkyl and aryl halides, sodium, and tin tetrachloride react to form a series of compounds of the formula R_nSnX_{4-n}. The reaction can be performed by preparing the sodium alkyl or aryl (*32, 38*) and then adding the tin tetrachloride or by simultaneous reaction of all of the reactants (*16, 18, 44*). A number of variations of the basic reaction have been described. Because the reaction goes through several steps, none of which is unique, it is not possible to make pure $RSnX_3$, R_2SnX_2, or $RSnX_3$ compounds, and frequently it is difficult to obtain complete alkylation to R_4Sn compounds. The basic reaction is useful to obtain a crude product for further synthetic manipulation.

$$RCl + 2Na + SnCl_4 \rightarrow 2NaCl + RSnCl_3 \quad (1)$$

$$RSnCl_3 + RCl + 2Na \rightarrow 2NaCl + R_2SnCl_2 \quad (2)$$

$$R_2SnCl_2 + RCl + 2Na \rightarrow 2NaCl + R_3SnCl \quad (3)$$

$$R_3SnCl + RCl + 2Na \rightarrow 2NaCl + R_4Sn \quad (4)$$

By-product reactions:

$$R_2SnCl_2 + 2Na \rightarrow R_2Sn + 2NaCl \quad (5)$$

$$2R_3SnCl + 2Na \rightarrow R_3Sn - SnR_3 + 2NaCl \quad (6)$$

$$2RCl + 2Na \rightarrow R - R + 2NaCl \quad (7)$$

$$\text{Solvent} + RCl + Na \rightarrow R - \text{solvent} + NaCl \quad (8)$$

$$2RCH_2CH_2Cl + 2Na \rightarrow RCH{=}CH_2 + RCH_2Cl_3 + 2NaCl \quad (9)$$

$$SnCl_4 + 2Na \rightarrow SnCl_2 + 2NaCl \quad (10)$$

In the synthesis of butyltins, the optimum reaction is obtained when a slurry of finely dispersed sodium in a hydrocarbon solvent reacts with butyl chloride and tin tetrachloride under carefully controlled conditions of temperature. This is not as simple as it sounds because the heat of reaction is considerable and the heat transfer with cooling media available is not too good. The degree of control should be as close as possible: A variation of only 2°C. will result in an appreciable shift in the amount of by-product formed. A great deal of work is indicated in the patent literature on controlling by-product formation by various modifications of this basic reaction. Luijten and van der Kerk (*38*) and Ramsden and Gloskey (*49*) indicated that there are less by-products when a lower alkyltin is further alkylated than when tin tetrachloride is alkylated.

This process depends on:

$$RSnCl_3 + 3RCl + 6Na \rightarrow R_4Sn \quad (11)$$

$$R_2SnCl_2 + 2RCl + 4Na \rightarrow R_4Sn \quad (12)$$

$$R_4Sn + SnCl_2 \rightarrow RSnCl_3 + R_2SnCl_2 + R_3SnCl \quad (13)$$

and then recycling part of the product.

The basic Wurtz reaction is applicable to almost all simple alkyl and aryl chlorides. Among its many disadvantages are: degradation of solvent through further alkylation or arylation; formation of high boiling hydrocarbon by-products; required control of sodium granulation; formation of R_2Sn and R_6Sn_2 compounds, which are difficult to convert to desired products economically; hazard of excess sodium, because any agent used to destroy excess sodium tends to also destroy some product; and difficult control temperature.

Grignard. The use of Grignard reagents to synthesize organotin compounds is rather old (*2, 24, 26, 31, 46*). However, the disadvantages inherent in a standard Grignard reaction have prevented its commercial utilization until recent modifications made it more feasible (*47, 48, 52*). The fundamental reactions are similar to those of the Wurtz system:

$$RMgCl + SnCl_4 \rightarrow RSnCl_3 + MgCl_2 \quad (14)$$

$$RMgCl + RSnCl_3 \rightarrow R_2SnCl_2 + MgCl_2 \quad (15)$$

$$RMgCl + R_2SnCl_2 \rightarrow R_3SnCl + MgCl_2 \quad (16)$$

$$RMgCl + R_3SnCl \rightarrow R_4Sn + MgCl_2 \quad (17)$$

By-product reactions:

$$2R{-}CH_2CH_2Cl + Mg \rightarrow RCH{=}CH_2 + RCH_2 - CH_3 + MgCl_2 \quad (18)$$

$$RCl + \text{solvent} \rightarrow R - \text{solvent} + HCl \quad (19)$$

The Grignard synthesis has been modified in several ways to effect a more economical and safer reaction. One modification uses an inert solvent instead of ether once the reaction has been started (*48*). In this case, all reactants are present simultaneously and the reaction may not be a true Grignard but more of a Wurtz type, where magnesium acts as the halogen acceptor in place of sodium. Another variation which extended the utility of the reaction utilizes tetrahydrofuran as the solvent (*42*, *52*) for the formation of arylic and vinylic magnesium chlorides and their subsequent reaction with tin tetrachloride. Prior to this work, the Grignard type synthesis was limited on a commercial scale to alkyltins because of the cost or lack of reactivity.

The Grignard synthesis with the recent modifications is now more flexible than the Wurtz synthesis and has the advantages of fewer by-products and higher yields. The disadvantages are still appreciable: relatively higher cost of magnesium as compared to sodium; hazard of ethers unless a nonetheral modification can be devised; and formation of higher boiling hydrocarbons.

Direct Reaction. Smith and Rochow (*53*) and others (*50*, *56*) have demonstrated that methyl chloride reacts with metallic tin to yield dimethyltin dichloride. This reaction is influenced by catalysts and requires a high temperature for reaction:

$$2CH_3Cl + Sn \rightarrow (CH_3)_2SnCl_2 \qquad (20)$$

There appears to be little, if any, redistribution of the methyl group during the reaction. Practically, the reaction is limited to methyl chloride (*53*). Although other alkyl chlorides will react, the temperature of reaction is such that most of the product is destroyed by pyrolysis in the reaction zone. Although the reaction is more general for alkyl iodides and bromides, these processes are not commercially feasible (*3*, *10*, *21*).

Miscellaneous Reactions. Other typical organometallic syntheses have been tried but none have appeared commercially feasible. Among these are the Meyer (alkali, alkyl chloride, and the lower valence form of metal chloride) (*36*, *45*), sodium-metal amalgam (*30*), calcium alkylation, aluminum alkylation, and Sandemeyer reaction (*27*).

Reactions

Pure Halides. The preparation of any pure organotin compound other than a tetraalkyl- or tetraaryltin depends either on complicated separations of mixtures of partially alkylated compounds, or on redistribution reactions, or both. The most universal reaction of organotin compounds is the redistribution of groups when the compounds are heated with tin tetrachloride (*18*, *20*, *25*, *44*). Varying ratios of reactants can be used, and the resulting products tend to conform closely to the idealized equations:

$$R_4Sn + SnCl_4 \rightarrow 2R_2SnCl_2 \qquad (21)$$

$$2R_4Sn + SnCl_4 \rightarrow 4R_3SnCl \qquad (22)$$

$$R_4Sn + 3SnCl_4 \rightarrow 4RSnCl_3 \qquad (23)$$

Actually, the reactions are very complex and all theoretically possible interchanges may occur, although some reactions appear to avoid forbidden states while others appear to go directly through the state (*38*). The reaction

$$R_4Sn + SnCl_4 \rightarrow 2R_2SnCl_2 \qquad (24)$$

does not go by direct successive alkylations (*12*), but rather

$$R_4Sn + SnCl_4 \rightarrow R_3SnCl + RSnCl_3 \qquad (25)$$

$$R_3SnCl + RSnCl_3 \rightarrow 2R_2SnCl_2 \qquad (26)$$

where R is butyl. The reaction

$$3R_4Sn + SnCl_4 \rightarrow 4R_3SnCl \qquad (27)$$

appears to go

$$R_4Sn + SnCl_4 \rightarrow R_3SnCl + RSnCl_3 \quad (28)$$

$$R_3SnCl + RSnCl_3 \rightarrow 2R_2SnCl_2 \quad (29)$$

$$2R_4Sn + 2R_2SnCl_2 \rightarrow 4R_3SnCl. \quad (30)$$

Vinyl- and phenyltins do not appear to conform to the alkyl reactions (*51*).

After redistribution of groups has been achieved, the major component can be purified from minor impurities by distillation, recrystallization, or sublimation.

Hydroxides and Oxides. Organotin halides hydrolyze in the presence of alkali to hydroxides and oxides (*9, 14, 15, 27, 28, 34*). As most organotin compounds are insoluble in water, complete hydrolysis of the halide frequency requires a dual solvent system, emulsion reactions, or prolonged reaction times.

$$R_3SnCl + OH^- \rightarrow R_3SnOH \rightarrow R_3Sn—OSnR_3 \quad (31)$$

$$R_2SnCl_2 + 2OH^- \rightarrow R_2SnO \quad (32)$$

$$RSnCl_3 + 3OH^- \rightarrow RSnO_2H \rightarrow RSnO_2^- \quad (33)$$

The R_3SnCl compounds yield both the hydroxide and the oxide derivatives. In some cases, such as the methyl and ethyl homologs, drastic methods are required to dehydrate the hydroxide to the oxide and the reverse hydration occurs spontaneously in the presence of moisture. Van der Kerk and Luijten report the formation of triethyltin hydroxide and its dehydration phenomena (*22*). E. L. Weinberg, Metal & Thermit Corp. Laboratory, has repeated the hydrolysis in a completely aqueous system. If the butyl homolog has been isolated, its existence has only been momentary and dehydration to the oxide is spontaneous. Dilute solutions of the butyl compound appear to contain some hydroxide form in equilibrium (*55*).

The R_2SnCl_2 compounds do not form dihydroxides but appear to dehydrate to the oxide. Bond angles require that such oxides be polymeric, and the character of the polymer is variable. Dibutyltin oxide is known in a toluene soluble form, which may be a ring trimer, and in a very slightly organic-soluble form of linear polymer of varying length (*19*). By residual water measurements, the length of polymer appears to vary from four to five units up to a large number when completely dehydrated.

Dialkyltin oxides also react with dialkyltin halide to form polymers with terminal halide groups.

The $RSnO_2H$ compounds, or stannoic acids, have not been investigated as thoroughly as the other derivatives (*9*). They are nearly neutral in reaction but will form salts which are sparingly soluble in water with strong alkalies.

Salts. Some salts of all three mixed forms of quadrivalent tin are known: R_3SnA, R_2SnA_2, and $RSnA_3$, where A is an acid anion. The method of preparation is the general metathetic reaction common to all organometallic compounds of this type:

$$R_2SnCl_2 + 2NaA \rightarrow R_2SnA_2 \quad (34)$$

$$R_2SnO + 2HA \rightarrow R_2SnA_2 \quad (35)$$

$$R_2Sn(OR')_2 + 2HA \rightarrow R_2SnA_2 \quad (36)$$

Common salts are the acetates, laurates, stearates, maleates, and benzoates.

Sulfur Derivatives. Like other organometallic compounds, hydrogen sulfide and mercapto-substituted organic molecules react with organotin chlorides or oxides to form mercapto derivatives (*33, 57, 58*):

$$R_2SnCl_2 + 2HSR' \rightarrow R_2Sn(SR')_2 \quad (37)$$

$$R_2SnO + 2HSR' \rightarrow R_2Sn(SR')_2 \quad (38)$$

Miscellaneous Derivatives. Organotin oxides react with aldehyde and ketone to yield acetals and ketals (*7*). They also undergo an unusual reaction with esters to

form an acetal-type product which will revert to the simple organotin salt of the acid part of the ester and the alcohol upon addition of water (*4*, *17*). This offers a novel but expensive method of hydrolyzing difficultly hydrolyzable esters.

Some dialkyltin salts of organic acids react with mercapto compounds to form complexes where the tin shows a valence of more than four. Although these compounds are unique, the only ones known are so complex that the exact structure is difficult to determine.

Other compounds, such as alkoxides, are known and are prepared in the classical manner (*39*). In all salt-type derivatives, the dialkyl organotins are capable of functioning in a polymeric manner to yield compounds of the following structure:

$$A{-}O{-}\left(\overset{R}{\underset{R}{Sn}}{-}O\right)_y{-}A$$

Halogen Acids and Halogens. In addition to the metathetic reaction of organotin oxides and hydroxides with halogen acids, many organotins will undergo dealkylation or dearylation under a variety of conditions (*35*):

$$R_4Sn + HCl \rightarrow R_2SnCl + RH \quad (39)$$

$$R_3SnA + HCl \rightarrow R_2SnACl + RH \quad (40)$$

$$R_2SnA_2 + HCl \rightarrow RSnA_2Cl + RH \quad (41)$$

The mono-organotin derivatives are resistant to halogen acid cleavage, and drastic conditions are required to effect any reaction. The radical bond strength follows the expected sequence, with alkyls being the most stable and aryls being the weakest.

Similar to the reaction of halogen acids, halogens react with organotin compounds to cleave organic groups (*13*, *29*, *40*):

$$R_4Sn + Br_2 \rightarrow R_3SnBr + RBr \quad (42)$$

$$R_3SnA + Br_2 \rightarrow R_2SnABr + RBr \quad (43)$$

$$R_2SnA_2 + Br_2 \rightarrow RSnA_2Br + RBr \quad (44)$$

The halogen reaction is frequently vigorous even with an alkyltin compound. The preferential removal of groups is in the same order as for halogen acids.

Properties

Except for the methyltin compounds and the salts of a few stannoic acids, organotin compounds are virtually insoluble in water. Even dimethyltin dichloride, which will form solutions in water over a wide range of concentrations, tends to separate when left undisturbed (*1*). A 20% solution, allowed to stand without agitation in a glass carboy, will separate to the extent that the solution at the top of the carboy is virtually free of the tin compound and the solution at the bottom is extremely concentrated.

Most organotin compounds are soluble to a considerable extent in almost all organic solvents. The aliphatic hydrocarbons tend to be the poorest solvents while alcohols, esters, ketones, and aromatic hydrocarbons are generally excellent. The principal exceptions are those compounds which have a polymeric nature, such as dibutyltin oxide which is virtually insoluble in all solvents and dibutyltin maleate which is soluble only in esters and high molecular weight plasticizers.

The physical properties of the organotin family run the gamut. In volatility, they range from the readily volatile tetramethyltin to the more difficultly distillable higher alkyl- and aryltin halides. Except for the tetraorganotins, the organotin halides, and the organotin salts of the lower molecular weight fatty acids, most derivatives undergo partial or total thermal decomposition in molecular stills at micron pressures.

Physiological Effects

The organotin compounds exhibit a wide spectrum of toxicity, with considerable variation from species to species. Tetrasubstituted organotins vary from tetraethyltin (*5, 54*), which approaches tetraethyllead in toxicity, to tetrabutyltin (*6*), which shows little acute oral toxicity in rats. Similarly, triethyltin chloride is extremely toxic (*59*), tributyltin oxide much less (*6*), and the octyl homolog still less (*54*). The disubstituted compounds show similar variations.

Variation in species is shown by dibutyltin oxide which has an LD_{50} of 100 to 200 mg. per kg. orally in rats (*6*) and an LD_{50} of about 2000 mg. per kg. orally in chickens (*23*). Human toxic reactions are known only in the case of diethyltin dioxide, which may contain some triethyl component and is believed responsible for the death of three people in France (*43*). Otherwise, although considerable objectionable symptoms have been reported, no fatalities are known. The most objectionable form of organotin compounds is the halide. The physiological reaction from the halide is not specific with the tin compound, but is general with any organometallic chloride which can form a hydrohalogen acid with water, either slowly or rapidly. The symptoms are smarting, burning, erythema, and edema. Prolonged contact may result in a second or third degree burn. The course of the reaction is similar to the organic arsine dichlorides, anhydrous hydrogen chloride, and hydrobromic acid. Some reactions have been noted in the industrial use of dialkyltin salts of acids. Generally these compounds are used at fairly high temperatures, and the symptoms tend to follow the pattern of the acid group, such as acetic, lauric, or maleic acid. Tributyltin oxide is a skin irritant in its own right, and its properties are similar to a hydrohalogen acid (*41*).

Commercial Uses

The first two commercial uses for organotin compounds were developed at about the same time during the forties and involved two classes of compounds. The General Electric Co. found that tetraphenyltin was well suited as a scavenger for hydrochloric acid, which would result if a short circuit occurred in a transformer that used their Pyranols or chlorinated diphenyls as coolants (*8, 37*). This application of tetraphenyltin is still growing. Somewhat earlier, considerable research on tin compounds had been undertaken coincidental with the development of tetraethyllead for use in gasoline. Research in the gasoline additive and lubricating oil additive field has been almost continuous since then.

The other commercial development involved the use of organotin chemicals as stabilizers for poly(vinyl chloride) against degradation caused by heat and/or ultraviolet light. The chemicals first commercialized for this use were dibutyltin dilaurate, dibutyltin maleate, and dibutyltin oxide (*60*). The consumption of organotins for this use has become substantial. Other materials are available, including a group of organotin compounds containing sulfur, which are most useful in the stabilization of rigid poly(vinyl chloride).

One of the most spectacular developments in this field used dibutyltin dilaurate as a major ingredient in anthelmintics for treating poultry (*23*). This application promises to grow further and undoubtedly will involve other compounds.

In the application of silicones to textiles and paper, such materials as dibutyltin diacetate and dibutyltin di-2-ethylhexoate are being used in increasing quantities as curing catalysts (*1*).

Much more recently, the commercialization of tributyl- and other trialkyltin compounds was begun. Basic research at the Tin Research Institute in England showed these materials to be of potential interest as fungicides and bactericides (*38*). This concept has been developed further, and several trialkyltin compounds are finding their way into commercial applications. The first application for tributyltin oxide was for the control of slime in paper and pulp mills (*41*).

A list of commercially available organotin chemicals will illustrate best their rapid and interesting rise into full scale production:

Dibutyltin dichloride	Dibutyltin sulfide
Dibutyltin oxide	Tributyltin sulfide
Dibutyltin dilaurate	Tributyltin oxide
Dibutyltin maleate	Tributyltin acetate
Dibutyltin diacetate	Tetraphenyltin
Dibutyltin di-2-ethylhexoate	

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Arylsilanes

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This investigation describes the study and development of methods of synthesis for the series of phenylbiphenylylsilanes, the characterization of these compounds, and the production of pilot plant quantities. Phenyltribiphenylylsilane, diphenyldibiphenylylsilane, triphenylbiphenylylsilane, and tetrabiphenylylsilane were produced by a sodium condensation method. The compounds have extreme thermal stability and several possible commercial applications are proposed.

It is somewhat unusual to find in the organosilicon field, where so much work has been carried out in the past 12 years, a class of silanes that have been almost entirely neglected. The tetraarylsilanes are such a class.

In this class tetraphenylsilane is the oldest known compound and of all the references pertaining to the tetraarylsilanes only two were found describing other compounds than the tetraphenylsilane (*28–30*).

The present investigation was undertaken to synthesize, characterize, and study the problem of pilot plant production of the complete series of phenylbiphenylylsilanes. The initial interest was in the unusual thermal stability of the silicon-aryl carbon bond and the low vapor pressure of the completely arylated silanes.

During this work Spialter, Priest, and Harris published their work on phenyl-*p*-biphenylylsilanes (*33*) which corroborated many of the values found in this investigation.

In general, all previous tetraarylsilanes have been prepared by the method of Polis (*26*) or some modification thereof. The equation for the preparation of tetraphenylsilane is typical of this method.

$$4C_6H_5Cl + SiCl_4 + 8Na \rightarrow (C_6H_5)_4Si + 8NaCl$$

The most notable modification is that of Schumb and Saffer (*30*), in which the alkylsodium is first prepared, subsequently added to the silicon tetrachloride, thereby giving a better distribution of organic groups. The sodium method is applicable to the synthesis of silanes which heretofore could be prepared only by the Grignard or alkylzinc methods.

Other possible methods of synthesis, such as the Grignard method, the "direct method," and the silane route (*25*), have been tried with varying degrees of success.

Taking into account that the method chosen would be subject to a considerable scale-up, it was decided to use the Polis method with modifications and with the incorporation of the new sodium dispersion techniques.

It was found early in the investigation that there were many variables which affected the reaction.

Discussion

Very briefly the variables which were found to affect the progress of these reactions to a marked degree were:

A. Sodium particle size
B. Solvent
C. Purity of reactants
D. Agitation
E. Temperature

The use of sodium dispersions, although not valuable in laboratory reactions, became exceedingly important in scale-up operations.

Because of the necessary scale-up, the selection of solvents became very important. An ether-type solvent has been proved to be the best for sodium reactions (*31*), with the diethers superior to the monoethers. Both diethyl ether and the dimethyl ether of ethylene glycol were tried experimentally and gave good yields. However, because of the flammability and the possibility of peroxide formation, these solvents were ruled out for large scale operations. VM & P high flash naphtha was chosen for scaled-up operations because of the following characteristics.

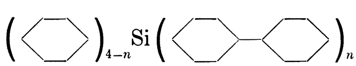
The boiling range is above the melting point of sodium.
It has a flash point above 50°F.
The products of reaction are soluble at reflux temperatures, but have negligible solubility at room temperatures.

It could therefore be used as a general solvent for all phases of the pilot plant method.

The reactions were found to be extremely sensitive to trace impurities present in the halogenated biphenyl and often completely inhibited the desired reaction. This difficulty was overcome to some extent by the use of high speed shearing type agitation.

The effect of excessively high temperatures was studied and found to lead to the coupling of the biphenyl molecules.

By giving proper attention to all of these variables the following general method was worked out and successfully employed with only a few exceptions. Sodium is dispersed under nitrogen, in VM & P high flash naphtha, in a specially designed unit. It is then transferred to the reaction kettle, and the chlorosilane and biphenyl halide, dissolved in high flash naphtha, are added slowly with efficient agitation. Heating under reflux is continued to complete the reaction and the hot mass is then filtered through a nitrogen pressure filter. The arylsilane is allowed to crystallize from the naphtha, then is filtered and dried. From this stage one recrystallization is usually sufficient to give nearly pure material. Yields are of the order of 65 to 80%. By this method the complete series of phenyl-*p*-biphenylylsilanes of the general formula given below have been prepared in quantity.



As of this writing several members of the series with *o*- and *m*-biphenyl have also been prepared and the synthesis of unsymmetrical silane molecules containing phenyl *o*-, *m*-, and *p*-biphenyl is under way. These reactions are sluggish, but can become violent if excessive amounts of reactants are allowed to build up.

Experimental

In general, pilot plant production followed laboratory findings. A flow diagram of the pilot plant unit is represented in Figure 1.

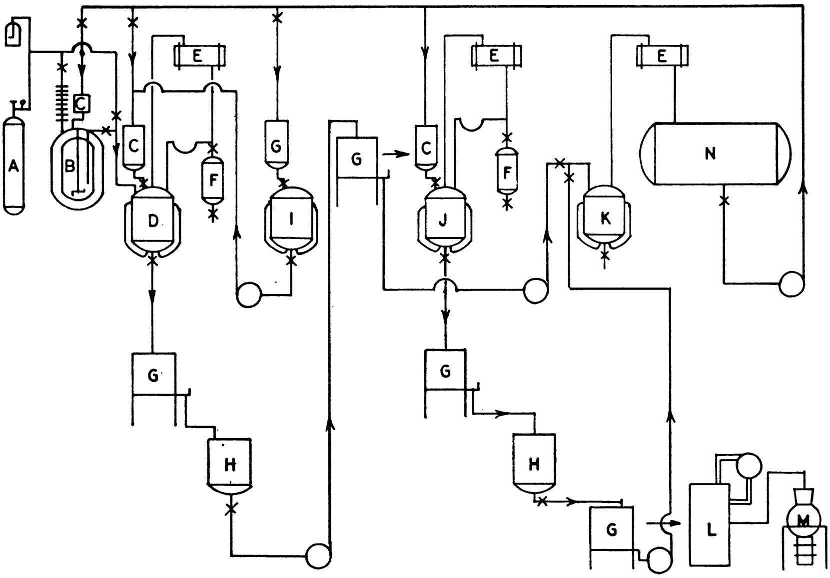


Figure 1. Equipment flow chart for phenylbiphenylylsilanes

A. Nitrogen cylinder
B. Sodium dispersator
C. Charge tanks
D. Reactor
E. Condensers
F. Receiver tanks
G. Filters
H. Crystallizing tanks
I. Solution make-up kettle
J. Purification kettle
K. Solvent recovery still
L. Drying oven
M. Pulverizer
N. Solvent storage tank
O. Solvent pumps

The following procedure for the pilot plant production of triphenyl-*p*-biphenylylsilane is typical of the series.

The reactor system, consisting of a specially designed sodium dispersator, *B*, reaction kettle *D*, and filter *G*, was purged with nitrogen until an Orsat analysis proved it free of oxygen. Six gallons of high flash naphtha and 11 pounds and 4 ounces of sodium were charged into the dispersion tank. The temperature was raised to 110° to 120°C. and the sodium dispersion was obtained by operating the dispersator head at 3500 r.p.m. for 15 to 20 minutes.

This dispersion was then transferred by nitrogen pressure to the nitrogen purged, previously warmed (70°C.) glass-lined Pfaudler kettle. This kettle was fitted with an air condenser, receiver, glass addition tank, nitrogen inlet, thermometer, dispersion inlet, and anchor-type agitator. A glass pipe was also extended nearly to the bottom of the kettle and it was fitted with a rubber suction bulb for drawing up a sample of the reaction mixture for observation. After the dispersion was transferred, the dispersion pot was rinsed with two 1-gallon portions of high flash naphtha and transferred by nitrogen pressure into the reaction kettle. The addition of the solution of halides in high flash naphtha was immediately begun and the initiation of the reaction, after the addition had started, was evidenced by a rapid rise in temperature and development of the characteristic blue colored reaction mixture. The addition was adjusted to maintain the reaction temperature at 120° to 130°C.

A reflux period of 4 hours followed after the addition was completed, and during this period 5 gallons of high flash naphtha was distilled over and removed. The hot refluxing reaction mixture was then filtered under nitrogen pressure. The filtrate was allowed to stand 3 to 4 days to crystallize the triphenyl-*p*-biphenylylsilane. The light yellow crystalline solid was filtered off, washed with 10 gallons of fresh high flash

naphtha, and dried in a steam-heated vacuum oven. The crude yield was 66 pounds, 71.5% of theory, melting point 153–6°C. One recrystallization from high flash naphtha gave white crystals of melting point 157° to 160°C.

The entire series of phenyl-*p*-biphenylylsilanes was prepared by similar procedures with results as listed in Table I.

Table I. Reaction Conditions

Product	Reaction Solvent	Melting Point of Crude, °C.	Crude Yield, %	Solvent Recovery	Melting Point of Purified, °C.	Purified Yield, %
$(C_6H_5)_3SiC_6H_4C_6H_5$	VM & P naphtha	153–6	71	VM & P solvent	157–60	56
$(C_6H_5)_2Si(C_6H_4C_6H_5)_2$		165–72	82		168–70	62
$C_6H_5Si(C_6H_4C_6H_5)_3$		150–63	62		156–58	54
$Si(C_6H_4C_6H_5)_4$		264–74	79	Xylene	278–282	72

To characterize these compounds a number of physical constants were determined (Table II).

Table II. Physical Properties of Phenylbiphenylylsilanes

Physical Properties	Tri-*p*-biphenylyl-phenylsilane	Di-*p*-biphenylyl-diphenylsilane	*p*-Biphenylyl-triphenylsilane	Tetra-*p*-biphenylyl-silane
Melting point, °C. KHS	174	170	159	283
Boiling point, °C.[a]	580	570	512	600
Flash point, open cup, °C.	380	338	299	400
Fire point, open cup, °C.	446	392	338	499
Density 20° C.	1.10	1.14	1.16	1.07
Surface tension, dynes/cm.				
350° F.	48.63	31.61	42.26	40.67
450° F.	43.86	28.91	38.47	39.50
Solubility, grams/100 ml. 20° C.				
Benzene	17.776	36.46	14.10	0.27
Methyl ethyl ketone	9.396	6.54	3.49	8.20
Ethyl alcohol	0.238	0.40	0.205	0.049
n-Heptane	0.052	0.38	0.799	0.096
Pyridine	2.725	12.91	17.88	16.69
Viscosity, cps.				
300° F.	40	8	370	solid
450° F.	1	1	12	500

[a] For comparison boiling points were included as determined by Spialter (*33*).

Practical Applications

With the determination of the physical properties complete, work on the applications of these materials is being carried out. The applications will depend primarily on the superior thermal stability, low vapor pressure, and excellent resistance to beta radiation of these compounds. Although new design and engineering work would be necessary, they may well prove adequate as extreme high temperature lubricants and hydraulic fluids needed for supersonic aircraft and guided missiles. For purposes of comparison, available aircraft hydraulic systems seldom reach temperatures in excess of 300°F., whereas planes and guided missiles beyond present prototypes will probably exceed the 700°F. range. The best of the commercially available oils, today, will not withstand temperatures above 550°F., whereas the phenylbiphenylylsilanes have shown no decomposition at temperatures well in excess of the 700°F. goal. More immediately, these compounds are being investigated as grease fillers, potting compounds, plastic stabilizers, and for many other applications where thermal and radiation stability are important.

Acknowledgment

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Alkanolamine Silicate Derivatives

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The synthesis and yield of alkanolamine silicates and their derivatives are discussed. These compounds exhibit unique properties such as dispersion and viscosity depression in nonaqueous systems. Tests and results are given for the effect of these properties on resins, rubbers, and paints.

Many data have been reported on the synthesis and chemical and physical properties of various organic silicates. Very little information, however, is available on the amino alcohol derivatives of the various silicic acids. Klein and Nienburg (*2*) prepared alkanolamine esters of orthosilicic acid by heating orthosilicic esters with monoalkanolamines in the presence of water. They observed that these compounds possessed some interesting pharmaceutical properties. A series of di-*tert*-butyl diaminoalkyl silicates was prepared and the properties were recorded by DiGiorgio, Sommer, and Whitmore (*1*), who synthesized these alkanolamine silicates by reaction of di-*tert*-butyldichlorosilane with various monoalkanolamines.

The physical and chemical properties of the various alkanolamine silicates were studied further by members of this laboratory. One or more of these silicates was expected to possess physical and chemical characteristics of commercial importance.

The alkanolamine esters of orthosilicic acid were prepared by the ester interchange method. Tetraethyl orthosilicate was heated with the calculated amount of amino alcohol in the presence of a catalyst. Some of the more basic amino alcohols, such as triethanolamine, required no catalyst to react with the orthosilicate esters. When the alkanolamine and alkyl orthosilicate would not react readily, catalytic amounts of sodium methoxide were added to initiate the reaction. The over-all reaction is represented by the following equation:

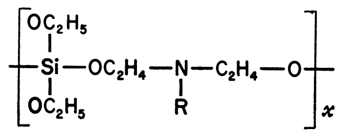
$$(C_2H_5O)_4Si + 4HOC_2H_4NR_2 \rightarrow (R_2NC_2H_4O)_4Si + 4C_2H_5OH \uparrow \quad (1)$$

An alternative method occasionally employed in the preparation of these esters used a dialkoxydichlorosilane in place of the alkyl silicate. This reaction is represented by the following equation:

$$(C_2H_5O)_2SiCl_2 + 4HOC_2H_4NR_2 \rightarrow (C_2H_5O)_2Si(OC_2H_4NR_2)_2 + 2HOC_2H_4NR_2\cdot HCl \quad (2)$$

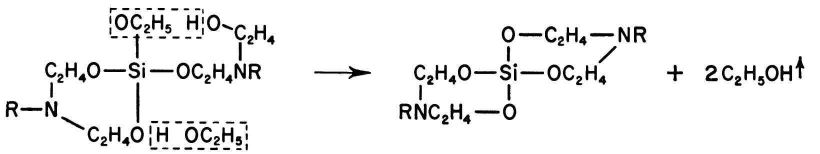
In the authors' experience, the ester interchange method is preferable, as it eliminates the filtration step required in the alternative procedure, and only half as much amino alcohol is needed.

The yields of both synthetic methods are good, but in the case of alkanolamine silicates prepared from the polyhydric alkanolamines, the reaction can continue until high polymers are formed (I).



I

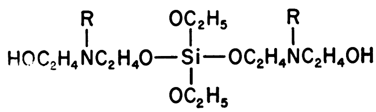
These compounds are very viscous liquids or solids, if cross linking occurs. A second side reaction is possible, which may account for a reduction in yield: The intramolecular reaction in Equation 3 can occur.

 (3)

II

Analytical data indicate that compounds of type II are formed during the reaction of a polyhydric alkanolamine and ethyl orthosilicate.

To get the maximum yield of the desired alkanolamine silicates (III)



III

the reaction must be terminated as soon as the theoretical amount of ethyl alcohol is removed from the reaction. In practice, slightly more than the theoretical amount of alcohol is removed. Subsequent analyses indicate that these polyhydric alkanolamine silicates are approximately 90 to 95% pure.

In Table I, a series of esters prepared from various β-alkylamino alcohols and tetraethyl orthosilicate is listed.

Table I. Properties of Various Alkanolamine Silicates

			% Calcd.		% Found	
Compound	Yield, %	B.P., °C./Mm.	Si	N	Si	N
$(C_2H_5O)_2Si(OC_2H_4NH_2)_2$	90	96–97/7.0	11.8	11.8	11.40	11.45
$(C_2H_5O)_2Si[OC_2H_4NH(C_2H_4OH)]_2$	98	—	8.74	8.74	8.9	8.54
$(C_2H_5O)_2Si[OC_2H_4N(C_2H_4OH)_2]_2$	100	—	6.76	6.76	6.62	6.71
$(C_2H_5O)_2Si[OC_2H_4NH(C_2H_5)]_2$	98	111/2.0	9.53	9.53	9.36	9.42
$(C_2H_5O)_2Si[OC_2H_4N(C_2H_5)_2]_2$	100	180/7.0	7.99	7.99	7.91	7.93
$(C_2H_5O)_2Si[OC_2H_4N(C_4H_9)_2]_2$	92	139–140/0.8	5.94	5.94	5.91	5.82
$(C_2H_5O)_2Si(OC_2H_4N[CH_2—CH(C_2H_5)—C_4H_9]_2)_2$	100	—	4.07	4.07	3.98	4.01
$(C_2H_5O)_2Si(OC_2H_4N[CH(CH_3)_2]_2)_2$	96	135/1.0	6.89	6.89	6.87	6.86
$(C_2H_5O)_2Si(OC_2H_4NH(C_6H_5)]_2$	96	118/0.3	7.18	7.18	7.10	7.15
$(C_2H_5O)_2Si[OC_2H_4N(CH)(C_2H_5)(C_6H_5)]_2$	95	138/0.2	6.29	6.29	6.28	5.98
$(C_2H_5O)_2Si[OC_2H_4NH(CH_2—C_6H_5)]_2$	100	135/0.3	6.28	6.28	6.19	6.22
$(C_4H_9O)_2Si[OC_2H_4N(C_2H_4OH)_2]_2$	96	—	8.65	8.65	8.86	8.48
$(C_3H_7O)_2Si[OC_2H_4N(C_2H_4OH)_2]_2$	95	—	6.34	6.34	6.21	6.19
$(C_2H_5O)Si[OC_2H_4N(C_2H_4OH)_2]_3$	93	—	5.42	8.13	5.41	8.07
$Si[OC_2H_4N(C_2H_4OH)_2]_4$	94	—	4.52	9.04	4.49	8.97
$(C_2H_5O)_2Si(OCH(CH_3)CH_2N[CH(CH_3)]_2)_2$	95	117–118/1.0	5.61	5.61	5.58	5.42
$(C_2H_5O)_2Si[OCH(CH_3)CH_2NH_2]$	98	110–111/6.0	10.51	10.51	10.21	10.32

A series of quaternary ammonium compounds prepared from dimethyl(triethanolamine) silicate and various fatty acids is listed in Table II.

Table II. Diethyldi(triethanolamine) Silicate–*N,N*-Dicarboxylates

Carboxylic Acid	% Calcd. Si and N	% Found	
		Si	N
Lauric	3.44	3.41	3.39
Palmitic	3.02	3.01	2.99
Stearic	2.85	2.79	2.82
Oleic	2.86	2.81	2.85
Ricinoleic	2.77	2.67	2.71
Linoleic	2.87	2.79	2.86
Eleostearic	2.87	2.81	2.84

Synthesis of Compounds

All materials were shown to be of acceptable purity before use. The tetraethyl orthosilicate and the various β-amino alcohols were supplied by Union Carbide Chemicals Co. They were checked for purity by distilling through a 30-plate Oldershaw column and were suitable for use without further purification. The fatty acids were obtained in the purest state available and were not purified further.

Diethoxydi(β-diethylaminoethyl) Silicate. A round-bottomed flask (5 liters), fitted with a Stark and Dean trap (Ace Glass, Inc., Vineland, N. J.) and a reflux condenser equipped with a calcium chloride drying tube, was used. In this were placed 238.9 grams (2.04 moles) of β-diethylaminoethanol and 212.5 grams (5.02 moles) of tetraethyl orthosilicate. A few boiling chips were added, and the mixture was heated until ethyl alcohol ceased to be evolved. The flask and its contents were cooled to room temperature and then attached to a vacuum distillation system. The residual ethyl alcohol was removed under vacuum at room temperature. The crude ester was purified by vacuum distillation. A colorless fraction of the pure ester boiling at 160° to 162°C. at 7 mm. under a nitrogen atmosphere was obtained. This fraction weighed 340 grams (95% of the theoretical amount).

Diethyldi(β-aminoethyl) Silicate. A three-necked flask (1 liter), fitted with a Trubore stirrer, a dropping funnel, and a reflux condenser equipped with a calcium chloride drying tube, was used. In it were placed 189 grams (1 mole) of diethoxydichlorosilane and 300 moles of dry benzene. The flask was immersed in an ice bath, and the contents were cooled to 5°C. The stirrer was started, and 305 grams (5 moles) of monoethanolamine were added dropwise at such a rate that the temperature did not rise above 20°C. When the last of the amino alcohol was added, the ice bath was replaced by a heating mantle, and the flask was heated to the reflux temperature of benzene for 1 hour to complete the reaction. The flask was cooled and the contents were filtered to remove the monoethanolamine hydrochloride formed during the reaction. The filter cake was washed twice with two 100-ml. portions of benzene, and the washings were added to the filtrate. The filtrate was vacuum stripped to remove the benzene and excess monoethanolamine. The crude ester was vacuum distilled under a nitrogen atmosphere for purification. The pure ester boiling at 96° to 97°C. at 7 mm. weighed 214 grams (90% of the theoretical amount).

Viscosity Characteristics in Nonaqueous Systems

The alkanolamine silicates and their quaternary derivatives with the fatty acids exhibit viscosity-depressant properties in nonaqueous systems. These characteristics are exemplified by the effects on the viscosity of suspensions of carbon in kerosine and of resins (Tables III and IV).

Table III. Viscosity of 1 to 1 Carbon-Kerosine Mixture[a] Containing Various Alkanolamine Silicates

Silicate	Concn., %	Required to Extrude 10 Cc. of Mixture through Rheometer	
		Time, sec.	Pressure, p.s.i.g.
Blank	—	545.0	2
$(C_2H_5O)_2Si[OC_2H_4N(C_2H_4OH)_2]_2 \cdot 2HOC_{17}H_{33}$	1	2.5	0
$(C_4H_9O)_2Si[OC_2H_4N(C_2H_4OH)_2]_2 \cdot 2HOC_{17}H_{35}$	1	3.9	0
$(C_2H_5O)_2Si[OC_2H_4N(C_2H_5)_2]_2 \cdot 2HOC_{17}H_{35}$	1	10.5	0
$(C_2H_5O)_2Si[OCH(CH_3)CH_2NCH(CH_3)_2]_2 \cdot 2HO_2CH_{17}H_{33}$	1	5.6	0

[a] Carbon was Thermax, 0.25 to 0.5 micron (Thermatonic Carbon Co., New York, N. Y.).

Table IV. Effect of Alkanolamine Silicates on Resin Viscosities

Resin Type	Viscosity at 27° C., Centipoises		
	No additive	1% A[a]	1% B[b]
Epoxy	8000	6000	6000
Phenolic	800	500	560
Styrene	340	300	260
Styrene acrylate	7540	4500	3900

[a] A is diethyldi(triethanolamine) silicate.
[b] B is dibutyldi(triethanolamine) silicate.

Effects in Resins. Besides the viscosity effects cited above, these silicate materials affect the flow characteristics of resins. Both the extrudability and injection molding characteristics are improved by the addition of the silicates. The data obtained from these tests are shown in Tables V and VI and Figure 1. Two filled resins, one a vinyl and the other a phenolic, were tested by the following procedure.

The vinyl resin was ground (through 10 mesh) with a Wiley rotary knife mill (Arthur H. Thomas Co.). Samples were prepared by adding 0.5 gram of each additive to separate 50-gram portions of the milled resin, followed by mixing with a mortar and pestle. Additional mixing occurred when the test specimens were injection molded at 325°F. to make preformed slugs 3/8 inch in diameter and 1 inch in length for use in the flow measuring apparatus.

The phenolic resin samples were prepared by adding 0.5 gram of each silicate to separate 50-gram portions of the resin, followed by mixing with a mortar and pestle. Test specimens 3/8 inch in diameter and 1 inch in length were preformed at room temperature and a pressure of 10,000 p.s.i.

The apparatus for the flow tests is a constant force, vertical-orifice machine consisting essentially of the orifice, block, charge chamber, ram, and pressure system. A split cone containing a vertical orifice 1/8 inch in diameter and 2¼ inches in length is clamped into a steam-heated block. Within the block, below the orifice and concentric with it, is the charge chamber which is 3/8 inch in diameter and 2 inches in length. The ram is so arranged that it applies pressure to the charge chamber from

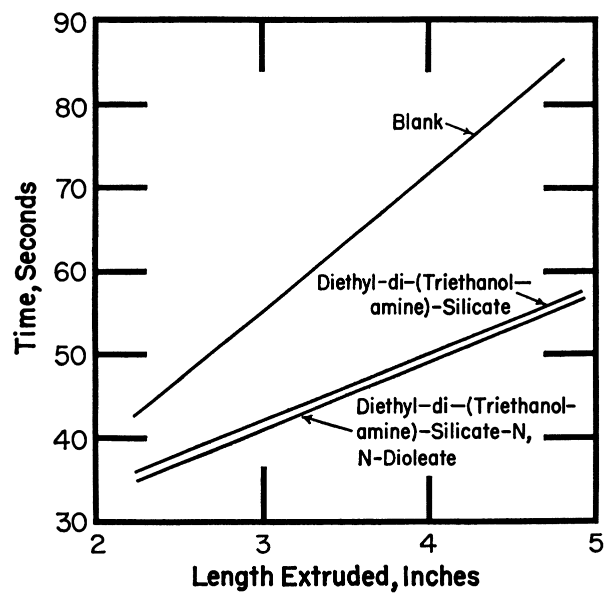


Figure 1. Extrusion rates of a vinyl resin through a 1/8-inch orifice

the bottom, forcing the material up into the orifice. Variable pressure is applied to the ram by a mechanical system. Heat is supplied by steam passing through a reducing valve and into the block. The temperature is controlled by regulating the steam pressure.

The vinyl resin specimens at room temperature were inserted in a hot charge chamber at 300°F. and tested immediately. A pressure of 1400 p.s.i. was applied and the timer was started. The time required for the extrusion of the resin to the top of the die (2¼ inches in length) and for ½ inch intervals thereafter was recorded (Figure 1).

The phenolic resin specimens at room temperature were inserted in the hot charge chamber at 275°F. and tested immediately. A pressure of 1400 p.s.i. was applied and the timer was started.

After 2 minutes, the length of the extruded resin was measured. At the end of this time the resin within the charge was cured to a solid mass (Table V).

Table V. Length of Phenolic Resin Extruded

Additive, 1%	Mean Length, Inches
Blank	2.34
Diethyldi(triethanolamine) silicate	2.59
Diethyldi(triethanolamine) silicate–*N*-oleate	2.64
Diethyldi(triethanolamine) silicate–*N*,*N*-dioleate	2.82

Three resins polystyrene, Ethocel (Dow), and Vinylite UG-1800 (Bakelite Co.) were tested to determine the effect of the alkanolamine silicate on their injection molding characteristics. A Van Dorn injection molding machine (The Van Dorn Iron Works Co., Cleveland, Ohio) and a standard die were employed in testing these resins. The temperature of the mud cylinder was held constant and the pressure on the ram head was varied. The results are shown in Table VI.

Table VI. Effect of Diethyldi(triethanolamine) Silicate–*N*,*N*-Dioleate on Injection Molding Characteristics of Resins

Resin	Concn. of Silicate, %	Molding Temp., °F.	Pressure Required to Fill Mold in 1 Min., P.S.I.G.
Polystyrene	0	375	500
	1	375	400
Ethocel	0	375	525
	1	375	400
Vinylite	0	325	600
	1	325	475

Effects in Rubber. The alkanolamine silicate exhibit a pronounced effect on the compounding and curing of rubber. Tests were made on rubber stocks containing the compositions given in Table VII.

Table VII. Composition of Test Rubber Stocks

Ingredient	Blank[a]	Control	Experimental
Smoked sheet	100	100	100
M. P. C. channel black	500	50	50
Stearic acid	—	4	—
Alkanolamine silicate	—	—	4

[a] Parts by weight.

The silicates and smoked sheets of natural rubber were mixed in a Banbury mixer (Farrel-Birmingham Co., Ansonia, Conn.) for 6 hours at 145°F. Then half of the channel black was added to the rubber-dispersant mixture and mixing was continued for 2 hours. The rest of the channel black was added and mixing was continued 4 hours longer. The stock was dumped at the end of the 12-hour mixing cycle. The stock dumping temperature and the total power consumption during the mixing operation are tabulated in Table VIII.

From the Banbury mixing data, all the stock containing the silicates consume less power than the blank. Two of the stocks, Nos. 3 and 5, show very low power consumptions, much lower than stearic acid, which may indicate high lubricity and good tubing qualities.

Table VIII. Banbury Mixing, Surface, and Extrusion Data

Stock No.	Additive	Stock Dumping Temp., °F.	Power Consumed, Watt/Hr.	Surface Bloom	Stock Tack	Weight Extruded, G.	Length Extruded Feet	Length Extruded Inches
1	Blank	260	676	None	Slight	450	14	15
2	Control (stearic acid)	256	550	Considerable	None	448	13	6
3	Diethyldi(triethanolamine) silicate–*N*,*N*-dioleate	259	492	None	Slight	453	15	1
4	Diethyldi(triethanolamine) silicate–*N*,*N*-distearate	256	524	Slight	None	449	14	1
5	Dibutyldi(triethanolamine) silicate–*N*,*N*-dioleate	260	501	None	Considerable	456	14	5
6	Diethyldi(triethanolamine) silicate–*N*-oleate	259	588	None	Considerable	435	13	9
7	Diethyldi(triethanolamine) silicate	258	—	None	V. slight	446	14	0

The Banbury mixed stocks were sheeted off the laboratory mill after a 3-minute blending period and observed after 48 hours (Table VIII). All stocks had good general appearance, except No. 2 which was poor, and good visual quality of dispersion. Only stock 4 showed any surface bloom. Stocks 3 and 7 exhibited the most desirable tack.

When the sheets were off the mill 48 hours, the stocks were rewarmed on the laboratory mill and extruded through a Garvey die (G. R. Garvey & Sons, Hammonton, N. J.). The tube temperature was 180°C., the screw speed was 45 r.p.m., and the time of extrusion was 1 minute. The extrusion data are tabulated in Table VIII. All stocks were more effective than stearic acid as a lubricant, as indicated by the greater length extruded. Stock 3 was considerably more effective than stearic acid as a die lubricant.

Mooney plasticity tests indicated that none of the silicates had any softening action on rubber and that the silicates are essentially lubricants and not plasticizers for rubber.

The first three stocks, the blank, stearic acid, and stock 3, were cured to compare the physical properties of the stocks. The experimental stocks were taken and mixed with the ingredients in Table IX.

Table IX. Ingredients for Cured Rubber Stocks

Ingredient	Parts by Weight
Experimental material	154.00
Zinc oxide	5.00
B L E[a]	1.00
Pine tar oil	3.00
Sulfur	3.00
Mercaptobenzothiazole	0.75

[a] Antioxidant for rubber (Naugatuck Chemical Division of U. S. Rubber Co., Naugatuck, Conn.).

The stocks were cured at 274°F. for varying lengths of time. The physical properties measured during this test are tabulated in Table X.

Table X. Physical Properties of Cured Rubber Stocks

Stock	Time of Cure, Min.	Modulus 300%	Modulus 500%	Tensile, P.S.I.	% Elong.	% Set	Shore Hardness	Stock Gravity	*T*-50[a]
Blank	20	795	2050	3775	695	34	56	1.131	+13.1
Control (stearic acid)	30	1080	2630	4180	670	44	60	1.131	+6.7
	45	1330	2050	4450	655	49	64		−0.4
	60	1530	3330	4450	625	51	65		−5.3
	90	1810	3650	4490	585	50	68		−12.5
No. 3	20	1180	2850	4490	665	50	64	1.138	+1.0
	30	1390	3090	4470	650	55	67		−3.3
	45	1550	3340	4480	625	55	70		−8.8
	60	1620	3370	4320	605	56	70		−12.3
	90	1700	3420	4290	595	54	70		−14.2

[a] Temperature at which a specimen of rubber first becomes taut between the clamps.

The data in Table X show that silicate 3 has greater activation than stearic acid and develops equally as good maximum physical properties. Silicate 3 is much faster in curing than the blank. With as much activation as is shown by this silicate, the overcured physicals have held up well with no appreciable increase in modulus or reduction in ultimate elongation.

Dispersant Characteristics

In nonaqueous systems, the alkanolamine silicates and their derivatives exhibit dispersant effects. This effect is shown best by their action on the grinding properties of various pigments in paint vehicles.

Procedure. Data obtained with two pigments illustrate the behavior of these silicates in paints as dispersants: an easy grinding titanium dioxide pigment, Titanox-RA, manufactured by Titanium Pigments Corp.; and a more difficultly dispersible organic pigment, Pyrazalone Red, manufactured by Du Pont. For the paint vehicle in these tests, the authors used a modified alkyd resin, XA-C99, manufactured by the Sherwin-Williams Co.

The mechanical mixer employed in the dispersion tests was the Szegvari Attritor No. 01 (Union Process Co., Akron 8, Ohio). This instrument is essentially an accelerated ball mill employing ¼-inch steel ball bearings as the grinding elements. The Attritor was charged with 200 to 300 ml. of the pigment vehicle mixture, containing 1% by weight of the dispersant. The mixing was started and at 10-minute intervals a small sample was taken from the dispersion. This small sample was placed on a Hegman gage (Precision Gage & Tool Co., Dayton, Ohio) and the fineness of grind was determined.

Results. The fineness values obtained are plotted against the time of sample grinding. A curve is obtained for each paint composition. These experimental data are shown in Figures 2 and 3; each curve represents the average of several tests on a given paint composition.

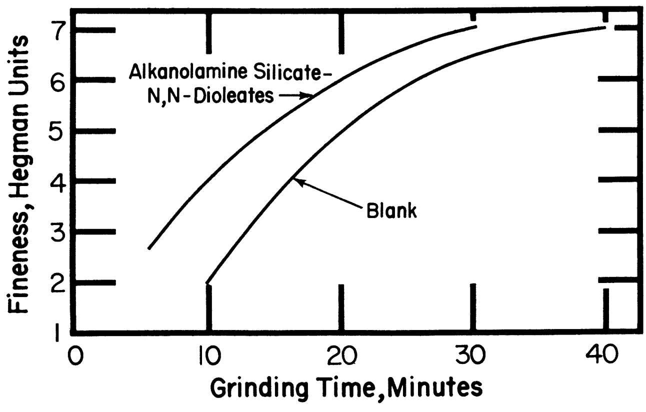


Figure 2. Grinding rate of Titanox-RA in an alkyd resin in the presence of alkanolamine silicates

Figure 2 represents the data obtained by dispersing titanium dioxide (Titanox-RA) in an alkyd resin (XA-C99). The charge added to the Attritor contained 150 grams of Titanox-RA, 147 grams of alkyd resin (XA-C99), and 3 grams of dispersant. The dispersants diethoxydi(triethanolamine) silicate–*N,N*-dioleate, diethoxydi(β-diethylaminoethyl) silicate–*N,N*-dioleate, and dibutoxydi(triethanolamine) silicate–*N,N*-dioleate are effective for this pigment-vehicle composition. Not only did the silicates give better dispersions, as indicated by the Hegman gage results, but they also dispersed the titanium dioxide more rapidly in the vehicle.

The blank, a test sample containing no dispersant, required 30 minutes of grinding in the Attritor to reach a fineness of 6.5. The silicate, added to the extent of 1 part per 100 parts of mix by weight, reduced the grinding time to 23 minutes. This reduction of 7 minutes represents a 23% decrease in the over-all grinding time.

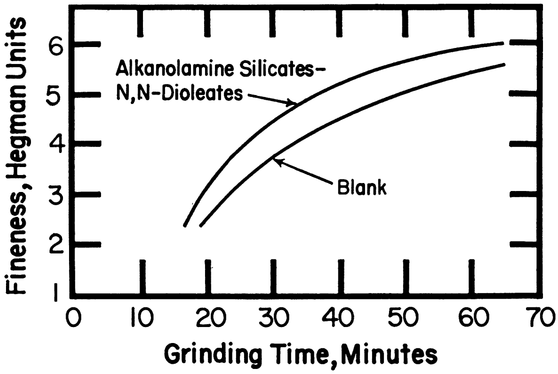


Figure 3. Grinding rate of Pyrazalone Red–Titanox-RA in an alkyd resin in the presence of alkanolamine silicates

The data in Figure 3 show the change in fineness with grinding time of paints containing 10% of the pigment as Pyrazalone Red. The paint tested contained 108 grams of Titanox-RA, 12 grams of Pyrazalone Red, 177 grams of alkyd resin, and 3 grams of dispersant.

The dispersant diethoxydi(triethanolamine) silicate–*N*,*N*-dioleate is very effective in dispersing the pigment mixture in its vehicle. After 65 minutes, the blank reached a fineness of 6.5, while the paint containing the silicate gave a fineness of 7 at the end of the same grinding period. The paint sample containing the additive attained a fineness of 6.5 in 43 minutes, whereas the blank took 65 minutes to reach this sample fineness. This difference of 22 minutes represents a 34% decrease in the grinding time.

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Alkyl Methoxysilane Water Repellents

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A new class of textile water repellents, of the non-durable type, is described. These compounds are long-chain alkyl methoxysilanes, a representative example being distearyl methoxysilane. Besides giving superior repellency performance, these compounds require no elevated temperature curing on the fiber and they give a superior hand to the fabric. Comparative performance data cover spray ratings, rain tests, permeability measurements, durability determinations, and practical service tests. Special attention is given to the application of these new materials to dry-cleaned cloth, which may contain traces of dry-cleaning soaps and detergents.

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A series of improved water-repellent compounds has been developed which are suitable for use on textiles, paper, wood, leather, and other materials. They are silane derivatives of the general classes $(CH_3O)_2SiR_2$ and CH_3OSiHR_2 where R is a long-chain alkyl group containing 12 to 18 carbon atoms or more. A preferred compound of the group is distearyl methoxysilane, $(C_{18}H_{37})_2SiHOCH_3$, or a dimer or trimer thereof.

While other methods are available for making this compound on a commercial scale, a convenient method for making it in the laboratory is through the Grignard synthesis. The four steps in this synthesis are (1) conversion of stearyl alcohol to stearyl bromide or chloride, (2) reaction of the latter with magnesium to form the Grignard reagent, (3) reaction of the Grignard reaction with trichlorosilane, and (4) replacement of chlorine by methoxy. The equations are:

$$C_{18}H_{37}OH + HBr \rightarrow C_{18}H_{37}Br + H_2O \quad (1)$$

$$C_{18}H_{37}Br + Mg \xrightarrow[\text{ether}]{\text{dry}} C_{18}H_{37}MgBr \quad (2)$$

$$2C_{18}H_{37}MgBr + SiHCl_3 \rightarrow (C_{18}H_{37})_2HSiCl + MgCl_2 \quad (3)$$

$$(C_{18}H_{37})_2HSiCl + CH_3OH \rightarrow (C_{18}H_{37})_2HSiOCH_3 + HCl \quad (4)$$

The product is a white, waxy solid melting in the range between 165° and 170°C. It is insoluble in water, but readily soluble in such organic solvents as naphtha, petroleum ether, benzene, perchloroethylene, and carbon tetrachloride.

Formulas

Formulas for solutions used to impart water repellency to cloth are:

	I, %	II, %
Distearyl methoxysilane	30	5.0
Aluminum isopropoxide	3	0.5
Stoddard Solvent	67	94.5

Formula I is a concentrate or master solution which, when diluted with five volumes of Stoddard Solvent, gives Formula II. The latter is the working solution used in most of the tests reported below. The aluminum isopropoxide in these formulas serves to fix the silicon compound more firmly to the fabric being treated. It may be replaced, if desired, by other compounds such as butyl titanate or tetrabutyl orthozirconate. Aluminum soaps do not appear to work as well in this capacity.

Instead of dissolving the silicon compound in an organic solvent, as in Formula II, one may emulsify it in water, using an emulsifying agent such as ammonium or morpholine oleate, or cetyl dimethylbenzylammonium chloride.

Test Methods

The quality of fabrics treated with water-repellent finishes is determined by subjecting them to standard repellency tests, fastness tests, an air permeability test, and practical dry-cleaning tests. Out of a long list of possible tests the following six (*1*) were chosen for use in experimental work:

Method 1. Exploratory "Spray Rating" Test (for Repellency Evaluation). The test specimen, a 7 × 7 inch square piece of treated fabric, is fastened securely in the 6-inch metal hoop, and the hoop placed with the fabric face uppermost on the base stand. The flow of water down the fabric must coincide with the warpwise direction of the sample—i.e., the ribs of the fabric must be diagonal to the flow of the water running off the sample. Then 250 ml. of water of temperature 80° ± 1°F. is poured into the funnel and allowed to spray on the fabric. The duration of the spray is about 25 to 30 seconds.

At the completion of the spraying period the hoop is held by one edge, and the opposite edge tapped against a solid object. The hoop is rotated 180° and tapped once more to shake off loosely held water droplets.

After tapping, the spotted or wetted pattern is compared with standards. The fabric is assigned the rating of the standard to which it most nearly corresponds.

Method 2. Rain Test (for Repellency Evaluation). The standard drop penetration apparatus employed in the rain test is similar to that shown in (*1*). In the procedure an 8 × 9 inch test specimen is placed in the sample holder; then the sample holder with the fabric is placed on the 45° sample support in the path of the falling drops and a timing device is concurrently started. The water passes through the fabric, and is drained into a graduated cylinder where it is measured. The time required to collect 10 ml. of water in this manner is a relative measure of the resistance of a given specimen to the passage of falling drops.

A second way of determining the resistance of the fabric to falling drops in this method is to determine the amount of water passing through the fabric during 20 minutes. This latter procedure is the one employed most often in our tests.

Method 3. Wash Test (for Fastness Evaluation). A small "diaper washer" is filled with water at 160°F. The wash solution contains 0.25% soap, 0.1% sodium bicarbonate, and a little softening agent—for example, 0.1% Versene. The test fabric is placed in the washer with enough other fabric to make up the load recommended by the manufacturer (about 2 pounds of cloth).

The cloth is washed for 15 minutes, followed by three 5-minute rinses. The fabric is dried in an oven at 140°F. and ironed. It is allowed to stand overnight, and on the following day the fabric is put through the spray rating test.

Method 4. Solvent Extraction Test (for Fastness Evaluation). In a 1-pint bottle are placed 200 ml. of clean Stoddard Solvent and a test piece of fabric 7 inches

square. The bottle is capped and shaken for 30 minutes on a shaking machine. The cloth is removed, centrifuged to remove excess liquid, and dried in an oven at 140°F. The fabric is ironed and placed on a rack to age for 24 hours. After this period of time a spray rating test is run on the test fabric.

Method 5. Air Permeability Test. After the inner cylinder has been raised to the proper height, the sample piece of fabric is clamped securely between the orifice plates. The inner cylinder is released and the time required for 300 ml. of air to pass through the cloth is a measure of the air permeability of the fabric.

Method 6. Practical Dry-Cleaning Tests. Confirmatory practical tests were made by commercial dry cleaners.

Discussion

There is considerable need in the textile industry today for materials, either durable or nondurable, which can be applied to cloth to render it water repellent. These materials, besides being effective water repellents, should be easy to apply, and inexpensive, and should not decrease the air permeability or impair the hand of the cloth. In general, the nondurable repellents are sold either as naphtha-soluble concentrates to dry cleaners, or as water-emulsifiable pastes to textile mills. A few are sold in the form of dilute naphtha solutions in pressure cans, with Freon as the propellant, for use in the home.

The naphtha-soluble pastes are composed of a mixture of a wax and a naphtha-soluble aluminum salt such as aluminum stearate. The water-emulsifiable pastes are aqueous dispersions containing aluminum acetate or formate, emulsifying agents, and protective colloids in the continuous phase and a blend of waxes in the dispersed phase. Some silicone oils are also sold for use in naphtha solutions or water emulsions.

Nondurable water repellents are applied to the fabric by two general procedures: (1) The paste emulsified in water is applied by padding and is dried at a temperature around 250°F. in order to decompose the aluminum salt; generally a deposit of 2 or 3% active solids is sufficient to give satisfactory results. (2) The naphtha-soluble pastes are diluted with solvent to obtain the desired treating solution. The fabric is immersed in the treating solution with agitation for a short period, removed, and cured at 140°F. or lower. On new fabrics 2 or 3% active ingredients are sufficient for desirable results.

The naphtha-soluble water repellents are employed primarily by the dry cleaner, and the dry cleaner seldom treats new fabric with them. Usually a dry-cleaned garment contains a minute film of soap or detergent on the surface. Because these are wetting agents, and act in opposition to the water repellent, a large amount of wax must be put on the fabric to overcome their effect. Often 5 to 10% solids must be applied to the fabric to obtain even fair results, and 15 to 17% solids to obtain desirable results. Because of such limiting conditions as temperature, costs, and equipment, the dry cleaner cannot use durable repellents. Also, he cannot employ water-emulsion type of nondurable repellents for fear that excessive shrinkage of garments might occur during the treating process. The only products available to the dry cleaner are often the naphtha-soluble nondurable pastes.

The materials studied in this investigation are silane derivatives or low order silicones. Because they contain long alkyl hydrocarbon chains they are, in a sense, a hybrid of a wax and a silicone, both of which are known to have hydrophobic or water-repellent properties. By combining them in the same molecule it was hoped to produce substances more repellent than either parent substance, and cheaper than the pure silicones. By having easily hydrolyzable hydrogen or methoxy groups on the silicon nucleus, it was hoped to achieve curing of the water repellent on the fabric at room temperature. Many classes of silane derivatives were synthesized and tested, in the quest for materials which would prove effective when used in low concentrations. Alkyl chains containing more than 12 carbon atoms were found to be necessary, prefer-

ably 16 to 18. Two such alkyl groups worked better than one or three. Branching or unsaturation in this carbon chain was deleterious.

Results

Exploratory Spray Rating Tests. The effect on several types of cloth of distearyl methoxysilane repellent, in comparison with various textile water-repellent compositions used commercially by the dry-cleaning industry, is shown in Table I. These

Table I. Spray Rating Tests on Commercial Water-Repellent Compositions

Repellents	Concn.[a]	Khaki Oxford (New)	Raincoat Formula[b] Khaki Oxford	Khaki poplin	Brown poplin	Rayon wool	Rayon gabardine	Charged System[b] Khaki Poplin
A	1 : 9	90	70	80	100	80	90	0
B	1 : 3	100	90	90	100	80	90	80
C	1 : 8	90	50	70	100	70	80	0
D	1 : 10	50	0	0	100	80	80	0
E	1 : 8	90	70	70	90	70	50	0
F	100%	50	0	0	70	50	50	0
G	1 : 7	70	70	70	100	90	90	0
H	1 : 5	90	70	70	100	80	100	0
Formula II		100	100	100	100	100	100	90

[a] Recommended by manufacturer.
[b] See text.

results have only qualitative significance. The treating solutions were prepared by the methods prescribed by the manufacturers. The fabrics were added to the treating solutions at the rate of 30 pounds of fabric per 100 pounds of solution and were immersed for 5 minutes. The fabric was removed and extracted until the weight increase was 15 to 20% of the weight of the fabric; this required about 12 seconds. After extraction the fabric was tumbled for 30 minutes at 140°F. The fabric was pressed and hung in an atmosphere kept at 70°F. and 65% relative humidity for 24 hours before testing.

In this easy test, ratings of 90 or 100 are to be considered good, 80 is fair, and 70 or below is poor. Table I shows that many repellents perform reasonably well on new cloth. They work better on some types of cloth than on others and they are generally less effective on cloth which has been dry-cleaned and which contains residual traces of dry-cleaning soaps. Different dry-cleaning methods leave behind different amounts or types of such soaps. No one commercial repellent is satisfactory on all types of cloth. Formula II has given uniformly excellent results in this test; 100 ratings are obtained with such varied types of fabric as cotton shirting 3.65, cotton poplin 5.90, wind-resistant cotton poplin 6.75, Indian Head cotton 4.85, wind-resistant cotton Oxford 9.00, Dynel 8.08, linen 3.30, linen 6.50, nylon 3.20, rayon 4.55, rayon-gabardine 6.75, 60 to 40 rayon wool 10.90, silk 1.98, and pants fabric wool 6.64. The numbers above refer to weights of fabric in ounces per running yard of yard-wide material.

The standard methods used for dry-cleaning the fabrics merit some description. In the raincoat formula, an emulsion consisting of 1 part of Cyclo Soap (dry-cleaning soap supplied by R. R. Street and Co.), 1 part of Stoddard Solvent, and 1 part of water was added at the rate of 3 ounces for each pound of fabric, and 1 gallon of Stoddard Solvent. Then Buckeye paint remover (manufactured by Davies Young Soap Co.) is added at the rate of 0.6 ounce per pound of fabric to be cleaned. The fabric is added, and the load is run for 20 minutes, after which the solvent is drained from the machine. The machine is filled with fresh solvent and the load rinsed for 20 minutes. The fabric is extracted and is tumbled at 140°F. for 30 minutes to remove the last traces of solvent.

In the charged system, the washer containing Stoddard Solvent is charged with 0.75% by volume of a synthetic detergent (886 sold by R. R. Street and Co.). The fabric is added at the rate of 1 pound of fabric per pound of solvent, and then 1 ounce of water per pound of fabric is added. The machine is run for 30 minutes, employing

constant filtration. At the end of the filtration cycle the washer is drained and refilled with fresh solvent. The load is rinsed for 10 minutes and extracted. After extraction the fabric is tumbled at 140°F. for 30 minutes.

Rain Tests. A more difficult test for a water repellent to pass is the rain test. Here water droplets fall onto the treated cloth from a height of 3 to 10 feet, depending on the type of cloth used, and the amount of water is measured which passes through the cloth in a given length of time. Many repellents exhibit good spray ratings, but show up very poorly in the rain test. Figures 1 and 2 show the results obtained with

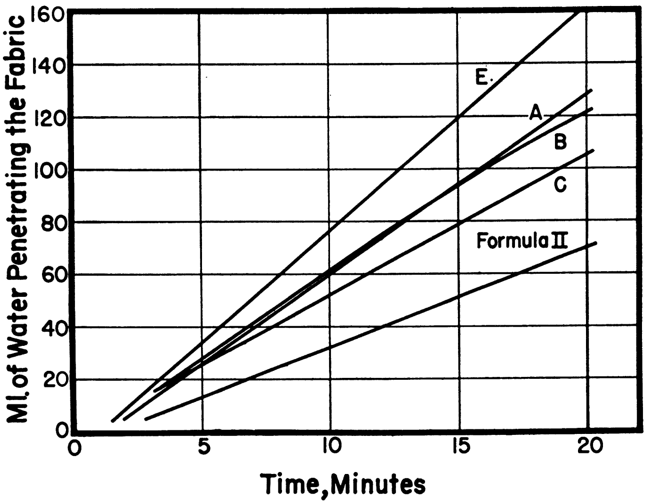


Figure 1. Rain test

Fabric. 60 to 40 rayon-wool
Head of water. 5 feet

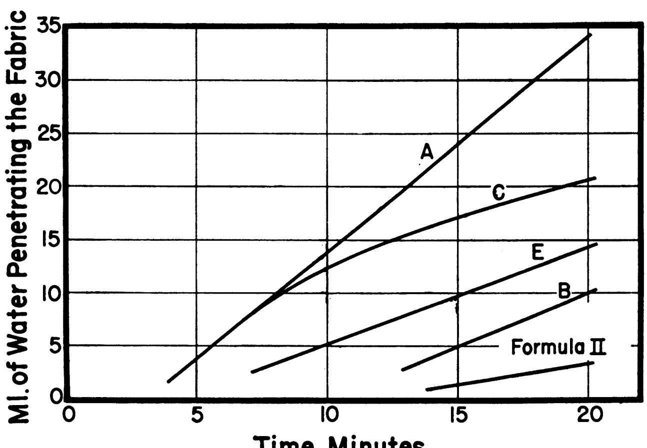


Figure 2. Rain test

Fabric. 7-ounce, cotton Oxford (dry cleaned)
Head of water. 5 feet

a new 60 to 40 rayon-wool and a dry-cleaned cotton Oxford (7 ounce) fabric, both under a 5-foot head of water. Aside from Formula II, the products tested are probably the largest selling nondurable repellents used by the dry-cleaning industry.

Air Permeability Tests. It is not difficult to treat fabric so that it sheds water, even in a rain test apparatus, if the pores in the fabric are clogged. In evaluating water-repellent compositions, it is, therefore, important to measure their air permeability after the water-repellency treatment has been applied to the cloth. The results of tests on cotton Oxford cloth are shown in Table II. None of the products clogs the

Table II. Air Permeability of 7-Ounce Khaki Oxford Fabric

Repellent Used	Time to Pass 300 Ml. of Air, Sec.	Reduction, %
None	26	—
A	26	0
B	28	8
C	29	12
E	29	12
J	54	107
K	31	20
Formula II	28	8

pores excessively except product J, and possibly product K. Other types of cloth give similar results in this test.

Fastness Tests. The durability of repellent-treated fabric samples was tested by subjecting them to wash tests described in Method 3. Attempts were made to remove the water-repellent films by washing with Stoddard Solvent as well as with soap and water. Spray ratings were determined on the fabric samples both before and after the washings.

Table III. Effect of Washing and Dry Cleaning of Treated Fabrics

Repellent Treatment	Spray Rating Values		
	Treated cloth	After wash	After dry cleaning
B	100	50	70
Formula II	100	50	70
Zelan	100	100	100

Zelan is a water repellent of the durable type; Formula II is a repellent of the nondurable type.

Practical Dry-Cleaner Tests. In order to get experience with commercial practice, samples of repellent treatments from various dry-cleaning establishments in the Cleveland, Ohio, area were secured. Rayon gabardine fabric was obtained, which, as shown in Table I, column 8, is an easy material to make water repellent. Several yard lengths of this cloth were sent to each of several cleaners with instructions to clean and treat

Table IV. Commercial Treatments in the Cleveland Area

Water-Repellent Product Tested	Cloth Cleaned and Treated by Authors (Raincoat Formula)	Cloth Cleaned and Treated by Local Dry Cleaners[a]	Cleaned by Outside Cleaner, Treated by Authors	
			Charged system	Raincoat formula
Formula II	100	—	100	100
A	90	—	80	90
B	90	80, 100	90	90
C	80	80, 80	80	80
G	90	90, 0	70	90

[a] Results from two different cleaners.

them as described in Table IV. (Only those cleaners participated who disclosed the particular water-repellent products used.) On receipt of the treated cloths, spray rat-

ing tests were made. Column 3 shows that the water-repellent treatment being sold by some dry cleaners is not very effective, particularly when it is remembered that this is an easy fabric to treat. The zero result in column 3 suggests that the cleaner cleaned the cloth, but did not give it the water-repellent treatment.

Further practical application tests have been made by arrangements with a dry cleaner, to treat 50-pound batches of various fabrics after cleaning them by either the raincoat formula or the more widely used charged system. The water repellency of these materials was then tested in the laboratory. The repellency values have been uniformly higher than those given by commercial nondurable repellents, and the hand of the treated fabric was good.

Preparation of Distearyl Methoxysilane

In a 12-liter flask, fitted with a stirrer, a gas inlet tube which reaches nearly to the bottom of the flask, and a reflux condenser, is placed 5000 grams (18.5 moles) of octadecyl alcohol. A thermometer is suspended inside the condenser so that the bulb is below the surface of the alcohol. The alcohol is heated to 100°C., and dry hydrogen bromide is passed in at 100° to 120°C. until no more absorption occurs (about 2 hours). The crude octadecyl bromide product is transferred to a separatory funnel, separated from the aqueous hydrobromic acid formed during the reaction, and shaken with one third its volume of concentrated sulfuric acid to remove the unreacted alcohol. The lower acid layer is drawn off and discarded. The residual bromide is mixed with an equal volume of 90% methanol and aqueous ammonia is added with intermittent shaking until the solution is alkaline to phenolphthalein. The lower bromide layer is drawn off and washed once with 90% methanol. It is then dried with calcium chloride, filtered, and distilled. The yield of the octadecyl bromide product, boiling at 213° to 216°C./14 mm. mercury, is 5360 grams (87% of theory).

In a 5-liter, 3-necked flask fitted with a stirrer, separatory funnel, and a condenser equipped with a calcium chloride tube, is placed 100 grams of magnesium turnings. A small crystal of iodine and about 100 ml. of anhydrous ether are added. Then 100 ml. of a mixture of 1330 grams (4 moles) of *n*-octadecyl bromide and 2 liters of dry ether is added. Localized heating may be applied to start the reaction, if desired, and after it has started, the rest of the bromide-ether mixture is added over a period of 1 to 2 hours, as determined by the rate of reflux. After complete addition, the mixture is refluxed for another hour to ensure completion of the reaction. Finally, it is diluted with an additional 2 liters of anhydrous ether for use in the next step.

In a 6-liter, 3-necked flask equipped with a dropping funnel, mercury-sealed stirrer, and a reflux condenser equipped with a calcium chloride tube, are placed 67.7 grams (0.5 mole) of trichlorosilane and 2 liters of dry benzene. Stirring is commenced. Through the dropping funnel is added 312.5 grams (1 mole) of *n*-octadecyl magnesium dissolved in a liter of ether—i.e., the product from the foregoing paragraph. This addition is made over a period of 2 hours, at a temperature below 30°C. The contents of the flask are stirred for an additional hour to complete the reaction. Then 48 grams (1.5 moles) of methanol is added dropwise so as not to let the temperature rise above 30°C., which requires an additional 2 hours. Then the flask is heated to 70° to 80°C., while a stream of dry nitrogen is passed over the surface. Heating and stirring are continued until evolution of hydrogen chloride ceases; this requires about 6 hours. The contents of the flask are then cooled and filtered. The filter cake is washed twice with two 50-ml. portions of dry benzene. The filtrate is fractionated at atmospheric pressure to remove the benzene, methanol, and residual ether. An oily fraction which distills at 160° to 225°C./3 mm. is removed and discarded. The product, an amber-colored liquid at elevated temperatures, is poured into a flask, stoppered, and allowed to cool. At room temperature it is a white solid melting at 65-67°C.

	Found on Analysis, %	Calculated for $(C_{36}H_{74}SiO)_x$, %
Carbon	77.3	78.4
Hydrogen	13.5	13.5
Silicon	5.8	5.1

The molecular weight by ebulliometry was 1120, so that, in the formula $(C_{36}H_{74}SiO)_x$, the value of x is 2.0, indicating slight polymerization.

Literature Cited

(1) Federal Standard Stock Catalog, Supt. Documents, Washington 25, D. C., Section IV, Part 5, CCC–T–191a. pp. 8, 12, 22, 23, 24, supplement, Oct. 8, 1945.

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Redistribution of Organochlorosilanes

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The chemical groups bonded to silicon can be caused to redistribute to form new substituted silane species. Prior work, describing such reactions of inorgano-, organo-, and mixed silanes, is reviewed. Some of these redistributions can be of interest for the important commercial methods of manufacturing organochlorosilanes. The specific example of the methylchlorosilanes is discussed in this connection. Laboratory and pilot plant data obtained using a new catalyst, sodium chloroaluminate, for this reaction are presented. The advantages, preparation, activity, and life of the sodium chloroaluminate catalyst are also discussed.

Most organometallic compounds (of polyvalent metals) and many inorganic compounds undergo redistribution reactions—that is, the groups bonded to the central metal atom are capable of interchanging with substituents on another metal atom. Symbolically, this may be represented by

$$R{-}M + R'{-}M' \rightleftarrows R{-}M' + R'{-}M \tag{1}$$

This transfer or redistribution can occur between compounds containing metals of the same or of different species. Calingaert (*3*) has described a specific type of "redistribution reaction." Such reactions are characterized by zero heats of reaction and equilibrium constants which vary little with temperature and which are essentially determined by entropy changes. Only a limited number of organic reactions are known to fulfill these conditions.

The redistribution of groups attached to silicon is a very general phenomenon. Only a few types of these redistributions have been demonstrated to fall into Calingaert's classification. Most substituted silane redistributions appear to be equilibrium reactions, but usually the equilibrium is displaced and is not determined by entropy considerations alone. Interchanges are known to occur among organic, inorganic, and hydrogen groups bonded to silicon and the extant literature is discussed from this point of view. It is not the purpose of this paper to discuss silane redistributions involving other metal compounds (such as the Grignard or organozinc alkylations of chlorosilanes). The application of the redistribution of organochlorosilanes to their commercial synthesis will be described later.

Inorganic Redistributions

Although the halides of silicon have been known for many decades, it is only in recent years that a few studies have been undertaken with respect to their redistri-

bution chemistry. Forbes and Anderson (*29*) and Besson (*15*) have shown that mixed halogenosilanes can be made to undergo disproportionation at elevated temperatures. Thus, in the absence of catalysts:

$$ISiCl_3 \rightarrow ISiCl_3 + I_2SiCl_2 + I_3SiCl + I_4Si + Cl_4Si \tag{2}$$

The products formed in this reaction were in the correct statistical ratios to fall within the scope of the Calingaert redistribution reaction. A similar situation was found to prevail with the chloroisocyanates of silicon (*1*). However, chlorothiocyanates of silicon behaved differently (*2, 30*) in that the reaction

$$Cl_3Si(NCS) \xrightarrow{600°C.} SiCl_4 + Si(NCS)_4 \tag{3}$$

has an equilibrium constant of only about 0.1. This reaction was also found to proceed slowly at room temperature.

Halogenosilanes also undergo interchanges with alkoxy silanes. Thus triethoxychlorosilane and ethoxytrichlorosilane disproportionate readily at 100°C. (*49*). However, diethoxydichlorosilane is not changed under these conditions. Ethyl silicate and silicon tetrachloride redistribute (*23*) to form all possible chloroethoxysilanes. Different results are reported (*23*) with fluoroethoxysilanes in that triethoxyfluorosilane seems stable whereas the others disproportionate at room temperature. The easy disproportionation of diethoxydifluorosilane was not noted by Peppard, Brown, and Johnson (*39*), who were able to isolate this compound. Some of the results described above are beclouded by the fact that acids act as catalysts for these redistributions and that the side reaction

$$\equiv Si{-}O{-}C_2H_5 + \equiv Si{-}Cl \rightarrow \equiv Si{-}OSi\equiv + C_2H_5Cl \tag{4}$$

is reported to occur (*49*). These types of redistributions have also been demonstrated to occur where the alkoxychlorosilanes have organic or hydrogen groups bonded to the silicon (*3, 35*). It was concluded that such organo groups increase the stability of the corresponding alkoxychlorosilanes.

Very little has been done on the interchange of alkoxy groups bonded to silicon. It has been found that different alkyl silicates can react with each other to form all possible combinations of silicates (*40, 42*). These alkoxy redistributions are catalyzed by both aluminum chloride and aluminum ethoxide.

The redistribution of hydrogen and halogen atoms attached to silicon is among the most facile to effect. Trifluorosilane disproportionates even at liquid nitrogen temperature (*17*) and the other fluorohydrogensilanes are also readily redistributed (*24*). No added catalyst was found necessary to redistribute diiodosilane (*25*). However, catalytic techniques are necessary for hydrogen-chlorine interchanges. Aluminum chloride (*26, 48, 51*), organic nitriles (*9*), and dialkylcyanamides with (*11*) or without (*10*) metal halide promoters have been used successfully. All of these catalysts have also been used where organic groups are bonded to the silicon. The reactions involved in this type of redistribution do not lead to a statistical distribution of all the possible products. Alkoxy groups are similar to halogens in their ability to interchange with hydrogen atoms in silanes. Basic types of catalysts such as sodium metal (*31*) and alkali metal alkoxides (*4, 7, 34*) have been generally used, although metal halides are also applicable (*26, 27*). All the work done has been on the disproportionation type of reaction and no attempts have been made to establish the existence of an equilibrium state.

Organic Redistributions

The reactions discussed heretofore have not been concerned with the transfer of organic groups from one silicon compound to another where such transfers involve carbon-silicon bonds. That such rearrangements can occur was demonstrated in 1874

by Ladenburg (*37*). He showed that the alkylation of phenyltrichlorosilane resulted in a diphenylsilicon compound

$$C_6H_5SiCl_3 + Zn(C_2H_5)_2 \rightarrow C_6H_5Si(C_2H_5)_3 + (C_6H_5)_2Si(C_2H_5)_2 + Si(C_2H_5)_4 \quad (5)$$

A similar type of phenomenon was also observed (*22*) when in the course of some hydrogenation studies at 300°C. rearrangements of silicon-bonded organic groups were found to occur.

$$2C_2H_5Si(CH_3)_3 \rightarrow (C_2H_5)_2Si(CH_3)_2 + Si(CH_3)_4 \quad (6)$$

These incidental observations were the forerunners of the work done by Calingaert and coworkers (*19, 20, 33*), concerning the redistribution reaction of organosilanes. They studied the specific reaction of tetraethylsilane and tetrapropylsilane catalyzed by aluminum chloride at 180°C., and showed the formation of the statistically calculated amounts of all the possible ethylpropylsilanes. Others, working with this reaction (*32*), have obtained no evidence for the isomerization of the propyl groups during their transfer.

The organohydrogen silane redistributions investigated to date have all involved phenyl groups. Thus phenylsilane redistributes at room temperature, with aluminum chloride, to give good yields of tetraphenylsilane and silane (*47*).

$$4C_6H_5SiH_3 \rightarrow (C_6H_5)_4Si + 3SiH_4 \quad (7)$$

Phenylmethylsilane, $(C_6H_5)(CH_3)SiH_2$, and phenylchlorosilane, $C_6H_5ClSiH_2$, under the same conditions yield products which indicate that the phenyl, hydrogen, and methyl or chloro groups all shift around during the redistribution. Under somewhat modified experimental conditions, however, phenyldichlorosilane is reported (*50*) to yield only dichlorosilane and diphenyldichlorosilane:

$$2C_6H_5HSiCl_2 \rightarrow (C_6H_5)_2SiCl_2 + H_2SiCl_2 \quad (8)$$

that is, the chloro groups do not redistribute at all. Benkeser and Foster (*13, 14*) have shown that with a sodium-potassium alloy as a catalyst all the phenyl hydrogen silanes can be converted to tetraphenyl silane. Under these alkaline conditions methyl groups did not redistribute. Phenylpotassium was, therefore, postulated to be an intermediate in this type of redistribution:

$$(C_6H_5)_2SiH_2 + K \rightarrow C_6H_5K + (C_6H_5)H_2SiK \quad (9)$$

$$(C_6H_5)_2SiH_2 + C_6H_5K \rightarrow (C_6H_5)_3SiH \quad (10)$$

$$(C_6H_5)_3SiH + C_6H_5K \rightarrow (C_6H_5)_4Si \quad (11)$$

The last major type of redistribution is that between organosilicon and chloro- or alkoxylsilicon. Alkoxy groups have been shown to interchange with aryl and alkenyl groups with sodium ethoxide catalysis (*5, 6, 8*). Under these mild reflux conditions, the saturated alkyl groups do not shift.

The phenylchlorosilanes have been found to disproportionate slowly with basic catalysts (*14, 36*) to form tetraphenylsilane. The reverse reaction apparently also proceeds. Although it was earlier stated (*41*) that tetraphenylsilane did not react with silicon tetrachloride at 300°C., a subsequent patent (*28*) showed the formation of phenylchlorosilanes from these reactants.

Most of the previously discussed redistribution reactions are of academic interest only. The methylchlorosilane redistributions, however, appear of commercial importance. This situation prevails for several reasons. First, the methylchlorosilanes are the largest group of chemicals used in the preparation of silicones for commercial exploitation. Secondly, two of the commercially available methods of manufacturing methylchlorosilanes—(1) the direct process of methyl chloride with silicon and (2) the Grignard process of methyl chloride with magnesium and silicon tetrachloride (*43*)—result in complex mixtures of all the possible methylchlorosilanes

$$\begin{array}{l} CH_3Cl + Si(Cu) \searrow \\ \qquad\qquad\qquad CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl \\ CH_3Cl + Mg + SiCl_4 \nearrow \end{array} \qquad (12)$$

Because these species are not used in the same ratios in which they are produced, methods of interconverting or redistributing these by-products should be of economic importance.

The redistribution of methylchlorosilanes was first reported by Sauer and Hadsell in 1948 (*46*). They showed that the reactions proceeded at 250° to 450°C. under the influence of aluminum chloride. The redistributions were all equilibrium reactions, but deviated from the random nature stipulated by Calingaert's reactions. It was also found possible to methylate phenyl- and ethylchlorosilanes using the methylchlorosilanes. Zemany and Price (*52*) have studied the kinetics and thermodynamics of the reaction. They obtained the equilibrium constants for the reactions:

$$Si(CH_3)_4 + (CH_3)_2SiCl_2 \rightleftarrows (CH_3)_3SiCl \qquad K_{350} = 75 \qquad (13)$$

$$(CH_3)_3SiCl + CH_3SiCl_3 \rightleftarrows (CH_3)_2SiCl_2 \qquad K_{350} = 40 \qquad (14)$$

The reaction:

$$(CH_3)_2SiCl_2 + SiCl_4 \rightleftarrows CH_3SiCl_3 \qquad (15)$$

was too slow to be measured by their techniques. The redistributions were all homogeneous and gaseous. The rates varied linearly with the aluminum chloride concentration and were first order in chlorosilanes. The aluminum chloride was shown to be complexed with the chlorosilanes. The reaction mechanism postulated was first a rapid complexing of aluminum chloride with the chlorosilane, resulting in a weakened silicon-chlorine bond. Second, the reaction of the complex with another chlorosilane molecule to exchange a tetrachloroaluminate entity for a methyl or preferably for a chloro group. These methylchlorosilane redistributions were subsequently described in the patent literature. Both aluminum chloride, condensed phase (*12, 44, 45*), and sodium chloroaluminate, vapor phase (*16*), systems have been described.

Redistribution Catalyst and Equipment

The applicability of sodium chloroaluminate to the redistribution of the methylchlorosilanes has been studied in this laboratory. Both laboratory and pilot plant data have been obtained and the pertinent details thereof are described below. Although aluminum chloride functions as a catalyst for this purpose, it has certain inherent disadvantages. Because the methylchlorosilane redistributions using aluminum chloride are relatively slow, large volume or high pressure reactors and/or large concentrations of aluminum chloride are needed for a reasonable rate of production. These conditions are complicated by the volatility and ease of sublimation of the aluminum chloride which create handling and recycling problems. A relatively nonvolatile, more efficient catalyst would enable the use of a continuous process at relatively low or even atmospheric pressure. Preliminary experiments showed that sodium chloroaluminate is such a catalyst.

Sodium chloroaluminate is a solid which melts at 185°C. and is stated (*21*) to boil at about 800°C. Its vapor pressure–temperature relationships (*38*) indicate that some slight decomposition may occur at very high temperatures. Sodium chloroaluminate can be prepared by heating sodium chloride with aluminum chloride until a clear melt is obtained. For use as a redistribution catalyst, the sodium chloroaluminate functions best when deposited on an inert catalyst support. It has been found that large amounts of the sodium chloroaluminate can be adsorbed by such carriers as porous clay, Alundum, and silica. Despite the low melting point of the complex salt, no catalyst runoff has been observed even at 500°C. The catalyst-carrier combination

can be made by soaking the carrier in molten sodium chloroaluminate. A better technique, used for all the experiments described below is: (1) soak the carrier (¼-inch porous Alundum spheres supplied by the Norton Co., Worcester, Mass.) in a sodium chloride solution for several hours, (2) thoroughly dry the drained carrier at about 200°C., and (3) heat the carrier–sodium chloride with the appropriate molar equivalent of aluminum chloride at 250° to 475°C. in a closed vessel (the redistribution reactor may be used for this). This method results in a more uniform coating of sodium chloroaluminate on the carrier than does the soaking technique.

The effectiveness of sodium chloroaluminate as a redistribution catalyst was studied in several types of reactors. The earlier laboratory studies were done in a 2-inch glass tube, 2 feet long, heated by a Nichrome ribbon, and equipped with a dropping funnel, gas inlet, safety trap, condensing system, and thermocouple well extending into the center of the reactor. Larger scale experiments were done in a 4-inch-diameter, 3-foot-long steel reactor, similarly equipped.

A small scale pilot plant was set up for evaluating continuous operations. A diagram of the pilot plant is shown in Figure 1. The electrically heated reactor was

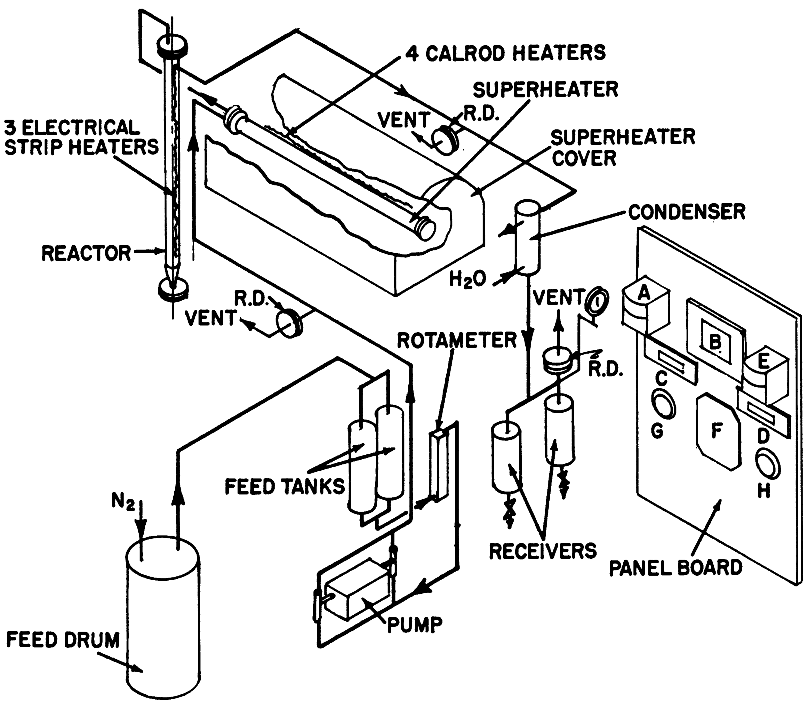


Figure 1. Pilot plant equipment

A. Superheater TIC
B. 6-point recorder
C. Superheater Limitrol
D. Reactor Limitrol
E. Reactor TIC
F. Reactor PRC
G. Superheater Variac
H. Reactor Variac

constructed of carbon molybdenum steel and was 4 inches in inside diameter and 5.8 feet long. The vaporizer-superheater was constructed of four consecutive passes of steel pipe, 4 feet long, enclosed in an electrically heated and insulated jacket. The

first pass of the heater was made of 1-inch pipe and was flanged at both ends to give access for cleaning. The following three passes were ½-inch pipe. The temperatures of both the reactor and vaporizer-superheater were controlled by use of Variacs and on-off temperature-indicating controllers. A pressure recorder controller and diaphragm-type control valve was used for regulating the pressure of the system. Temperatures were measured at the center of the reactor and at the outlet of the vaporizer-superheater. Temperature Limitrols were used as safety devices on both the reactor and the vaporizer-superheater to prevent overheating. The reactants were fed using a variable stroke reciprocating pump and feed rate was measured using a rotameter.

The operation of this pilot plant was carried out as follows. The organochlorosilane feed was pumped through the vaporizer-superheater at a controlled rate. The superheated feed then passed into the reactor through a dip tube leading to the bottom of the catalyst bed, then up through the bed, out of the reactor, and through the condenser to the receiver. Pressure was controlled by the pressure control valve in the vent line from the condenser. To maintain reactor pressure a small stream of nitrogen was bled into the vent line just upstream of the pressure control valve. In putting the system into operation the reactor was purged for several minutes with dry nitrogen. The nitrogen was then displaced by feeding reactants for a short time at atmospheric pressure. The system was then brought to operating pressure.

The methylchlorosilane compositions of both the feed and the product were quantitatively determined using mass spectrographic techniques. These results were checked occasionally by quantitative distillations. The various methylchlorosilanes used were materials produced by the Silicone Products Department, General Electric Co.

Results of Laboratory Studies

The first series of experiments (following those of an exploratory nature) was carried out in the 2-inch glass reactor in order to observe the effect of amount of catalyst in converting equimolar trimethylchlorosilane and methyltrichlorosilane to dimethyldichlorosilane. Simultaneously, temperature and residence time effects were studied. The results obtained for varying catalyst amounts (49 to 108 grams of sodium chloroaluminate per 1000 grams of Alundum carrier); temperatures (400°, 440°, 470°C.); and residence times (0.6, 1.2 minutes, calculated as the ratio of free space in reactor to the gas velocity) are given in Table I.

The averages (over all experimental conditions except 470°C.) for the per cent dimethyldichlorosilane formed with each batch of catalyst are plotted in Figure 2.

Table 1. Weight Per Cent Dimethyldichlorosilane Formed under Various Conditions

(Values determined by mass spectrometer assuming that only methylchlorosilanes are present in crude product)

	Temperature, °C.							
	400		440			470		
	Residence Time, Min.							
$NaAlCl_4$, G.	0.6	1.2	0.6	1.2	Means	0.6	1.2	Means
98	62	—	68	71	66.7	—	—	—
63	—	46	48	54	48.5	—	—	—
49	12	15	49	48	31.0	—	—	—
86	25	40	54	67	46.5	—	—	—
98	45	53	55	69	55.5	—	—	—
49	20	22	49	56	36.7	—	—	—
93	20	45	37	57	39.7	—	—	—
92	23	41	50	53	41.8	55	63	47.5
98	45	53	54	63	53.7	67	71	58.8
98	47	61	54	69	57.7	62	66	59.8
92	39	36	45	58	44.5	54	65	49.5
108	36	44	48	55	45.7	49	67	49.8
Means	35	43.5	50.9	60		57.4	66.4	

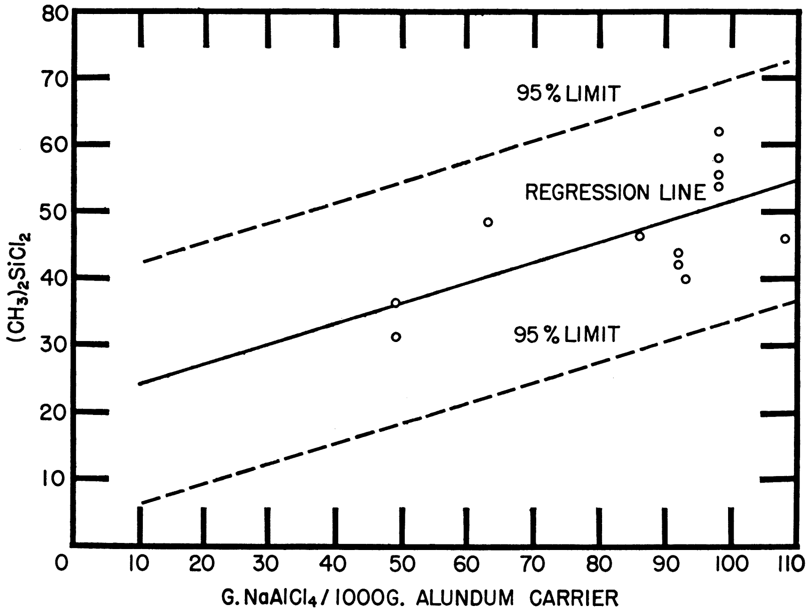


Figure 2. Effect of catalyst concentration

Although there is an appreciable scatter of the data, the calculation of the correlation coefficient indicates a linear relationship of the data plotted.

The effect of temperature on the rate of the redistribution is shown in Figure 3.

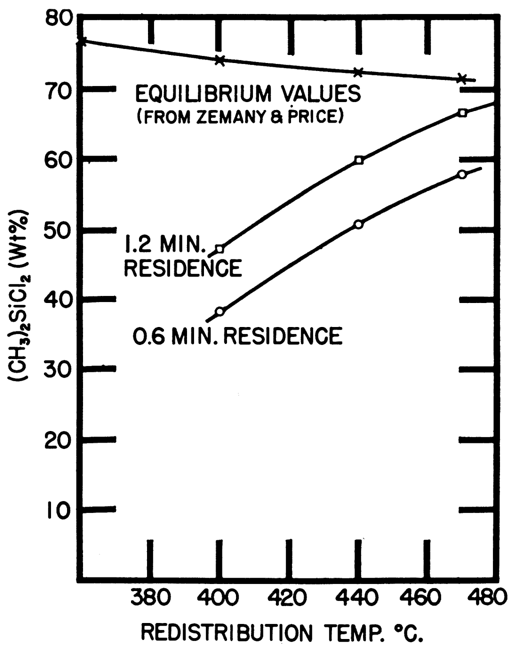


Figure 3. Effect of temperature at various residence times

Both the residence time and temperature have a marked effect on the extent to which the equilibrium values (of Zemany and Price) are approached. Analyses of the redistribution products indicated that the methyltrichlorosilane-trimethylchlorosilane ratio was equal to that of the feed. The various temperatures used affected both silanes similarly.

The effects of scaling up the chlorosilane redistribution process were investigated in the 4-inch steel reactor. By a suitable, statistically designed experiment it was possible to study the effects of temperature (400°, 430°, 460°C.), residence time (0.5, 1.0, 1.5 minutes), molar ratio of trimethylchlorosilane to methyltrichlorosilane in the feed (0.5, 1.0, 1.5), and catalyst life. The experimental design used was a 3^3 factorial confounded into three blocks (*18*). The experimental conditions and results are given in Table II.

Table II. Redistribution Conditions and Results for Confounded 3 × 3 × 3 Factorial

(Catalyst bed of 658 grams of $NaAlCl_4$ impregnated on 8600 grams of 1/4-inch Alundum spheres)

Blocks	Temp., °C.	Feed $(CH_3)_3SiCl$ / CH_3SiCl_3	Feed Rate, Ml./Hr.	Residence Time, Min.	Yield, %	$(CH_3)_2SiCl_2$ in Prod., %	Dup. Run Using 3% $AlCl_3$ in Feed $(CH_3)_2SiCl_2$, %	Trip. Run with No More $AlCl_3$ in Feed $(CH_3)_2SiCl_2$, %
I	400	0.54	917	0.5	96	9.9	— —	—
		1.04	297	1.5	99	33.1	— —	—
		1.56	489	1.0	98	24.6	— —	—
	430	0.54	484	1.0	95	31.6	— —	—
		1.04	914	0.5	90	35.8	— —	—
		1.56	293	1.5	82	62.0	— —	—
	460	0.54	312	1.5	90	40.5	— —	—
		1.04	449	1.0	91	56.2	— —	—
		1.56	880	0.5	98	50.4	— —	—
II	400	0.54	312	1.5	92	18.9	— —	—
		1.04	440	1.0	97	21.1	— —	—
		1.56	880	0.5	94	20.7	— —	—
	430	0.54	965	0.5	97	15.2	— —	—
		1.04	290	1.5	97	49.0	— —	—
		1.56	438	1.0	97	39.7	— —	—
	460	0.54	492	1.0	96	35.1	— —	—
		1.04	912	0.5	97	39.5	— —	—
		1.56	289	1.5	94	60.0	— —	—
III	400	0.54	482	1.0	95	12.6	17.9	32.3
		1.04	918	0.5	98	10.4	16.2	25.4
		1.56	288	1.5	96	48.8	37.2	45.1
	430	0.54	295	1.5	96	25.0	41.5	48.8
		1.04	471	1.0	97	30.7	40.3	42.8
		1.56	885	0.5	98	30.5	29.7	33.4
	460	0.54	980	0.5	94	19.7	38.1	49.1
		1.04	292	1.5	94	55.3	41.9	64.8
		1.56	437	1.0	98	55.6	52.0	63.0

An analysis of variance of the per cent dimethyldichlorosilane formed showed that all the main factors were very highly significant. The temperature, residence time, and feed ratio all influenced the extent of the redistribution. The block differences were also significantly different, indicating a lower extent of reaction with each successive block. The effective amount of catalyst was the only probable difference reflected by these blocks. The cause of this catalyst poisoning has not been elucidated, although experiments described below have shown that the catalyst can be regenerated.

The effect on the rate of the redistribution of the silane ratio in the feed is very interesting and is shown in Figure 4. Trimethylchlorosilane is more effective than methyltrichlorosilane in increasing the rate. This could mean that the trimethylchlorosilane is more readily adsorbed and activated by the catalyst carrier or that the methyltrichlorosilane is too strongly complexed by the catalyst to be very reactive. The extent of reaction, using the reported range in feed components, seems to be much larger than is accountable for on a purely mass action effect of methyl groups.

In this experiment, as in all those described using sodium chloroaluminate catalyst

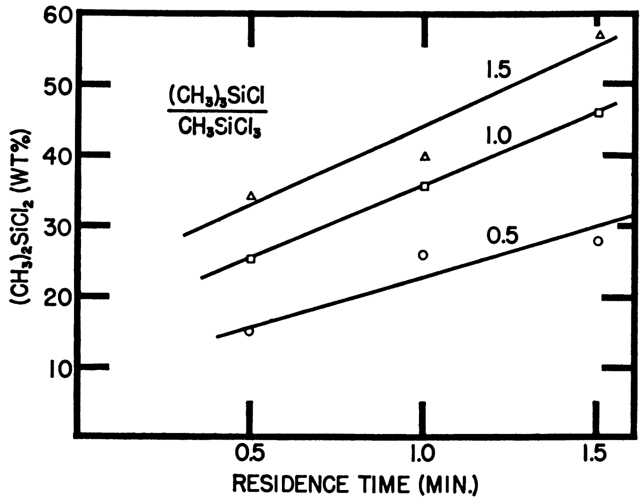


Figure 4. Effect of $(CH_3)_3SiCl/CH_3SiCl_3$ molar ratio in feed at various residence times

alone, none of the processing variables studied had any measurable effect on the yield of recovered product or on the ratio of methyltrichlorosilane to trimethylchlorosilane in the product. The amounts of undesirable by-products thus appear to be very small.

The apparent catalyst poisoning observed above could be due to (*a*) loss of sodium chloroaluminate by volatilization or solution; (*b*) slow decomposition of the complex to aluminum chloride which is lost by volatilization; or (*c*) decrease of active catalyst surface by plugging of the carrier pores or by coating of the carrier with a nonvolatile decomposition product. To evaluate some of these possibilities a study was made of the addition of aluminum chloride to a silane feed for passage over partially spent sodium chloroaluminate redistribution catalyst. The last block of nine experiments of the 3^3 design was repeated randomly using a feed with 3% aluminum chloride in each silane blend. A third repetition of this same set of experimental conditions was run, using the same catalyst batch, but with elimination of the aluminum chloride from the feed. The results of these experiments are included as the last two columns of Table II.

It is apparent from the results that the extent of the redistribution reaction was greater when aluminum chloride was used and apparently continued to improve when the final block of experiments was run. These conclusions were substantiated by the use of Student's *t* test. These preliminary results on the regeneration of the partially spent sodium chloroaluminate catalyst were confirmed and expanded in the continuous pilot reactor work.

Pilot Plant Results

Pilot plant studies were undertaken to determine the effects on the redistribution of pressure, continuous operation, and catalyst life. Methods for catalyst regeneration and alternate carriers for the sodium chloroaluminate were also investigated. Two series of statistically designed experiments were carried out mainly to study the effect of pressure. The pilot reactor (Figure 1) was used for these runs. The catalyst bed for each series consisted of 22 pounds of Alundum spheres impregnated with about 980 grams of sodium chloroaluminate sandwiched between 7-pound layers of untreated Alundum spheres. Conditions and results for these experiments are given in Tables

Table III. Effect of Pressure on Redistribution

(Confounded 3 × 3 × 3 factorial)

Block[a]	Pressure, P.S.I.G.	Temp., °C.	Residence Time, Min.	% $(CH_3)_2SiCl_2$ in Product
I	60	425	1	45
	100	425	2	63
	15	425	1.5	50
	15	475	1	51
	100	475	1.5	47
	60	475	2	48
	60	450	1.5	19
	15	450	2	26
	100	450	1	13
II	100	450	1.5	21
	15	450	1	20
	60	450	2	23
	100	475	2	24
	15	475	1.5	25
	60	475	1	13
	15	425	2	14
	100	425	1	5
	60	425	1.5	7
III	100	425	1.5	6
	60	425	2	11
	15	425	1	11
	15	450	1.5	20
	60	450	1	12
	100	450	2	14
	100	475	1	13
	15	475	2	25
	60	475	1.5	15

[a] Data listed in random order used.

Table IV. Effect of High Temperature and Pressure

Block[a]	Pressure, P.S.I.G.	Temp., °C.	Residence Time, Min.	% $(CH_3)_2SiCl_2$ in Product
I	180	475	5	74
	15	475	2	72
	15	550	5	68
	180	550	2	56
	15	550	2	58
	15	475	5	35
	180	550	5	51
	180	475	2	15
II	180	550	5	23
	15	475	5	21
	15	550	2	32
	180	475	2	11
	180	550	2	20
	15	550	5	45
	180	475	5	12
	15	475	2	14

[a] Data listed in random order used.

III and IV. Analyses of variance of the data showed that in both cases the loss in catalyst activity with time was very highly significant. The temperature effect was more pronounced in the 425° to 475°C. than in the 475° to 550°C. series. The differences in the amount of dimethyldichlorosilane were more significant in the 1- to 2-minute residence time range than in the 2- to 5-minute case. Higher pressure during the redistribution tended to give lesser amounts of product.

Table V. Characteristics and Performance of Catalyst Carriers

Composition	Alundum	Silica	Silica-alumina
Form	Spheres	Pellets	Pellets
Nominal size, inch	1/4	1/4	3/16
Bulk density, lb./cu. ft.	75	60	44
Specific surface,[a] sq. meters/g.	0.057	2.4	400
Catalyst absorption, lb. $NaAlCl_4$/cu. ft. carrier	6.5	22	18
Catalyst life, days to 60% $(CH_3)_2SiCl_2$ in product[b]	0.56	3.2	21

[a] N_2 absorption.
[b] 470°C., 100 P.S.I.G., and 5-min. residence time.

In addition to the Alundum spheres used as carrier in the above experiments, several other inert carriers were surveyed. Table V presents the properties of these carriers, and the results obtained for the specified operating conditions. The results of this survey indicated that higher surface area resulted in a slower decrease in catalytic activity for a given amount of exposure. However, the decrease in activity was still sufficient to warrant the investigation of methods for regenerating and sustaining catalytic activity. The results of such investigations using the Alundum carrier are presented below.

The need for a means of regenerating the sodium chloroaluminate was found to be somewhat fulfilled by using free aluminum chloride intermittently. When an equimolar methyltrichlorosilane-trimethylchlorosilane mixture was passed over a fresh sodium chloroaluminate bed in the pilot reactor (using conditions of 470°C., 180 p.s.i.g., and 5-minute residence time) the concentration of dimethyldichlorosilane in the product dropped to about 30% after 50 hours of operation. Doubling the residence time at this stage improved the rate of reaction somewhat, but only for a short while. When an amount of aluminum chloride equivalent to that in the catalyst bed was dissolved in the chlorosilane feed, there resulted a rapid attainment of equilibrium amounts of product. These results are shown in Figure 5. The regenerated catalyst

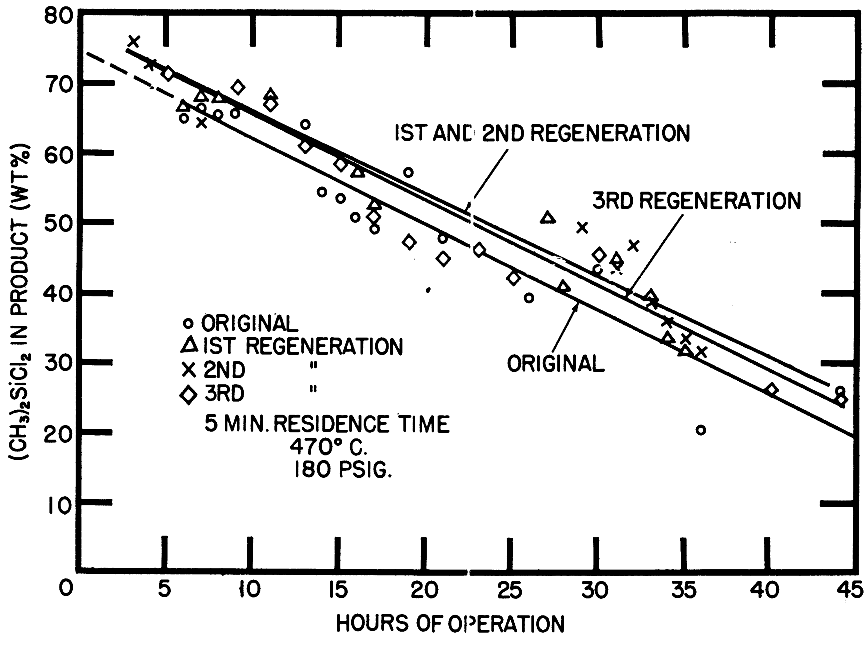


Figure 5. Effect of regeneration with aluminum chloride

bed began to lose its activity again after the aluminum chloride introduction was completed. The loss in activity occurred at a linear rate of approximately 0.9% less dimethyldichlorosilane per hour of operation. This regeneration process could be repeated periodically with similar results.

The over-all rate of production of dimethyldichlorosilane could be improved even more by the continuous addition of aluminum chloride to the feed stream. This was demonstrated by operating the reactor at 470°C., 100 p.s.i.g. pressure, and residence times of 2.5 and 5.0 minutes. Aluminum chloride concentrations ranging from 0.3 to 1.5 weight % of the methyltrichlorosilane-trimethylchlorosilane feed stream were

investigated. The results are shown, in the order obtained with a single batch of catalyst, in Table VI and are summarized in Figure 6. About 1% of aluminum

Table VI. Effect of Added Aluminum Chloride on Catalyst Efficiency

Residence Time, Min.	$AlCl_3$ in Feed, Wt. %	$(CH_3)_2SiCl_2$ in Product, Wt. %	Total Operating Hours
5.0	1.5	69	148
2.5	1.5	60	26
5.0	1.0	67	55
2.5	1.0	42	16
5.0	1.23	70	42
5.0	0.61	65	90
2.5	0.61	40	15
5.0	0.31	43	36
2.5	0.31	30	9
5.0	0.85	65	30

chloride dissolved in the feed stream appears to be optimum for the redistribution using sodium chloroaluminate. Larger amounts of the added halide tend to promote

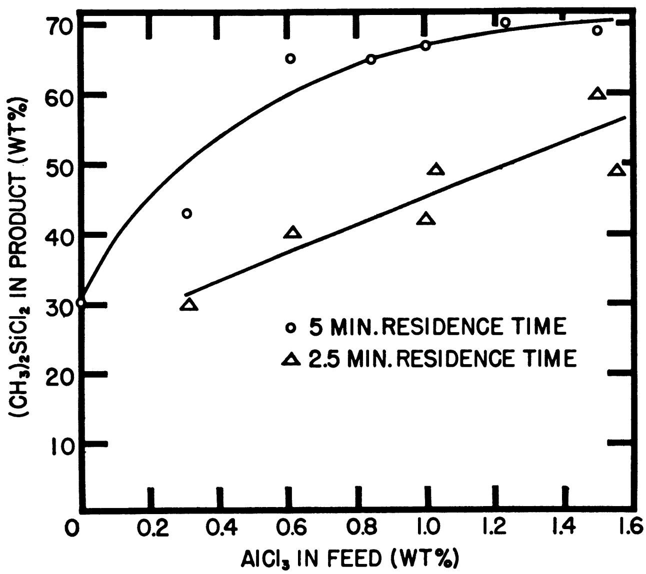


Figure 6. Effect of aluminum chloride promotion

the formation of excessive amounts of undesirable by-products. The total hours of sustained operation in this experiment were in excess of 500.

The contribution of the sodium chloroaluminate to the reaction was demonstrated by carrying out the redistribution in the absence of this complex. With 1 weight % aluminum chloride in the silane feed only 42% dimethyldichlorosilane resulted when either an empty reactor or a reactor filled with the inert carrier was operated at 470°C., 100 p.s.i.g., and 5-minute residence time. This is to be compared with a 68% yield using sodium chloroaluminate on the carrier.

Conclusions

The development work presented demonstrates the commercial feasibility of a process for the redistribution of methylchlorosilanes wherein sodium chloroaluminate impregnated on an inert carrier is used as catalyst. To sustain catalyst life small

amounts of aluminum chloride, included in the feed, were necessary. Operation with this catalytic system was found advantageous over the reaction catalyzed only by aluminum chloride. Because of the greater rate of catalysis the redistribution reaction can be carried out using relatively low pressures, and many of the difficulties inherent in the handling of gross amounts of aluminum chloride can be avoided.

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Direct Process for Preparation of Arylhalosilanes

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A practical method for the synthesis of arylhalosilanes is afforded by the high-pressure reaction of aromatic hydrocarbons with hydrogen containing halosilanes, as represented by:

$$C_6H_6 + HSiCl_3 \rightarrow PhSiCl_3 + H_2$$

This reaction proceeds under autogenous pressure at about 400°C. without a catalyst, or as low as 230°C. in the presence of a catalyst of the Friedel-Crafts type. The threshold temperature is further lowered, markedly, by organosubstitution of the halosilane and, to lesser degree, by substitution on the aromatic ring. As an example, in the reaction of methyldichlorosilane with benzene to produce methylphenyldichlorosilane, the threshold temperature is 130°C. These processes yield interesting by-products resulting from polyarylation of the silane as well as polysilylation of the aromatic nucleus. The synthetic method is described here in some detail and a possible siliconium ion reaction mechanism is considered in an effort to explain the nature of the products and by-products.

The industrially important field of organopolysiloxane chemistry was founded upon the Grignard process in the early 1940's. That process was versatile and afforded a ready route to the required organochlorosilane intermediates, but the raw materials were costly and the large amounts of solvent required made for a process of low volume efficiency. It was apparent that further growth of the infant industry would be materially facilitated by the development of direct methods for synthesis of intermediates.

The search for direct synthetic methods was rewarded by two major breakthroughs. The first, a result of work done simultaneously at General Electric Co. and The Dow Chemical Co., rested upon the reaction of methyl and phenyl halides with silicon metal at 300°C. to produce the corresponding organochlorosilanes (*2, 8–12*), the methyl compounds more efficiently than the phenyl.

The other direct process which has become commercially important for its wide versatility and good efficiency was the result of work initiated at The Dow Chemical Co., in November 1944, and continued at the Dow Corning Corp. This work embraced high pressure reactions of hydrogen containing halosilanes and organohalosilanes

of the types $HSiX_3$, $RHSiX_2$, R_2HSiX, with unsaturated hydrocarbons and benzenoid compounds. Alkylchlorosilanes so synthesized were reported in one communication (*3*) and in a series of patents (*5*), the first of which were applied for June 6, 1946. The preparation of arylchlorosilanes by this method was the subject of several patents (*1, 4*), the first of which were applied for June 6, 1946. This paper describes the fundamental observations that characterize this interesting method of synthesis.

Thermal Reactions in Vapor Phase

The reaction of benzene and trichlorosilane was first tried as a vapor-phase reaction at high temperatures. When mixtures of the two vapors were passed through a 3-inch × 10-foot iron tube at atmospheric pressure under varied conditions of temperature and contact time, with and without a variety of catalysts, only very small amounts of phenyltrichlorosilane were obtained. For example, a mixture of 6.6 gram-moles of trichlorosilane and 13.5 gram-moles of benzene was put through the tube packed with porous plate and the condensed effluent returned to a strip still from which the recovered reactants were recycled through the tube. After 43 hours at ca. 600°C., when 98% of the trichlorosilane had been consumed, only 0.52 gram-mole of phenyltrichlorosilane was obtained, with a large amount of by-product silicon tetrachloride and considerable brown, tarry still residue. Over half the benzene was recovered unchanged. Thus, the first approach to the problem was rather discouraging.

Thermal Reactions at High Pressures

Preparation of Phenyltrihalosilanes. Benzene-Trichlorosilane System. Autoclave reactions at moderately high temperatures and pressures afforded a more successful approach to the synthesis of arylchlorosilanes by the type reaction:

$$C_6H_6 + HSiCl_3 \rightarrow PhSiCl_3 + H_2$$

When mixtures of 18 gram-moles each of benzene and trichlorosilane were heated under autogenous pressures in a rotating 14.4-liter steel bomb, appreciable yields of phenyltrichlorosilane and phenyldichlorosilane were obtained at temperatures in the order of 400°C. The pressures ranged systematically from about 1300 p.s.i. at 350°C. to about 1900 p.s.i. at 500°C. The detailed data for several typical runs are summarized in Table I and represented in Figure 1, where yields of the desired phenyltrichlorosilane

Table I. Reaction of Trichlorosilane with Benzene

Charge. 1402 grams (18 moles) C_6H_6; 2460 grams (18.16 moles) $HSiCl_3$. 14.4-liter autoclave. 16-hr. reaction time

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	$SiCl_4$, Grams	C_6H_6, Grams	$C_6H_5SiHCl_2$, Grams	$C_6H_5SiCl_3$, Grams	Residue, Grams
PB—117	350	3688	1380	245	985	69	340	90
181	353	3763	1917	249	1324	0	48	26
116	375	3754	648	400	758	97	735	380
180	378	3772	1698	309	1152	48	293	55
142	378	3649	1634	278	1333	0	80	51
115	400	3793	514	498	815	150	968	382
179	403	3804	1060	648	1139	127	533	33
156	408	3687	1139	553	1309	37	188	34
114	425	3690	454	681	974	115	788	176
178	430	3643	713	617	922	206	999	120
177	454	3635	423	826	909	120	1075	144
99	465	3690	194	1218	1233	0	831	171
FCB— 78	505	3558	144	786	900	0	1038	570

are plotted as a function of temperature. The threshold temperature for the reaction is about 340°C. and the yield increases generally with temperature up to a limit. However, there is so much scatter in the recorded data, and additional data not tabulated but included in the plot, that a valid linear relationship may not be presumed. The most significant, yet admittedly generous, curve that might be drawn to show yield

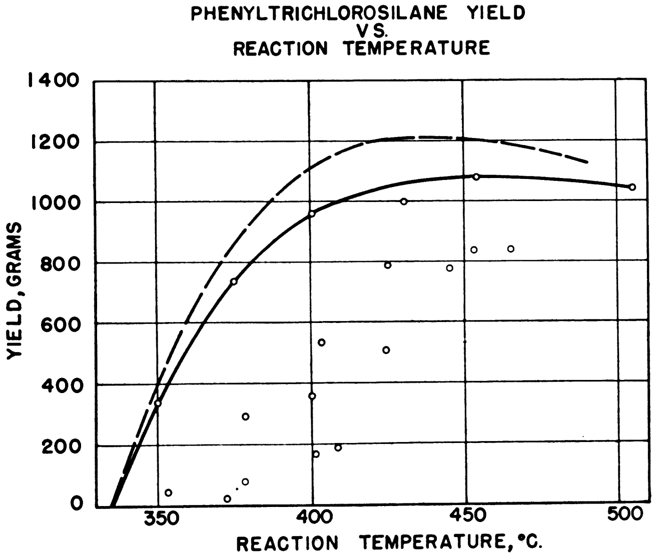


Figure 1. Thermal reaction of trichlorosilane with benzene

vs. temperature would envelop the data as shown by the heavy line of Figure 1. From this, it appears that the phenyltrichlorosilane yield approaches a limit of 1075 grams at about 450°C. (run 177). This amounts to 5.08 gram-moles or 33.8% theoretical (based on consumed reagent).

Some adjustment should be made for the by-product phenyldichlorosilane, because this compound, academically, represents silylation of the benzene and can be converted to a useful product, by rather simple means. If this by-product be so included in the yield plot, the dotted curve of Figure 1 is obtained. From this the optimum temperature for the reaction appears to be 430°C. Referring to the table, the pertinent run (No. 178) shows a yield of 4.72 gram-moles of phenyltrichlorosilane, which is 36.4% of theoretical, based on consumed trichlorosilane. Allowing for the 1.16 gram-moles of by-product phenyldichlorosilane, the total silylation yield becomes 45.3% theoretical.

The low yields are reflected in the large amounts of by-product silicon tetrachloride characteristic of this series. It is formed by thermal rearrangement of trichlorosilane (*13*):

$$4\ HSiCl_3 \rightarrow 3\ SiCl_4 + 2\ H_2 + Si$$

Accordingly, the 3.63 gram-moles of silicon tetrachloride of run 178 is equivalent to 4.84 gram-moles of the initial trichlorosilane. Thus, more of this reagent was consumed in the side reaction than was converted into the desired product, in nearly all runs.

With regard to materials balance in run 178, the phenyltrichlorosilane and phenyldichlorosilane account for 5.88 gram-moles or 95.6% of the 6.15 gram-moles of benzene consumed. These two products and the silicon tetrachloride account for 10.72 gram-moles or 83.2% of the 12.89 gram-moles of trichlorosilane consumed. These values might be benefited by some correction for the difference between bomb load and still charge, but because the discrepancy cannot be all attributed to mechanical losses, such correction cannot be properly assayed.

Small amounts of diphenyldichlorosilane were isolated from the higher boiling residues from these experiments. While sufficient for good characterization, the amounts obtained were too small to affect the materials balance significantly.

Benzene-Tribromosilane System. The analogous reaction of tribromosilane with benzene was demonstrated by autoclaving a mixture of 3 gram-moles of each for 16 hours at 490° to 510°C. Distillation of the product afforded 202 grams of phenyltribromosilane (0.6 gram-mole), the principal cut of which boiled at 94–9°C. and 2.3 to 2.9 mm. A little biphenyl was produced and, because of its close boiling point, contaminated the distilled product. The analytical data shown in Table IX are compared with the theoretical calculated on the basis of 6% such contamination.

Chlorobenzene-Trichlorosilane System. In the hope that chlorobenzene would react with trichlorosilane under less rigorous conditions than benzene and consequently afford a more efficient synthesis of phenyltrichlorosilane, a series of experiments was run in which 12 gram-moles of chlorobenzene and 24 gram-moles of trichlorosilane were bombed for 16 hours at varied temperatures and autogenous pressures. The data are

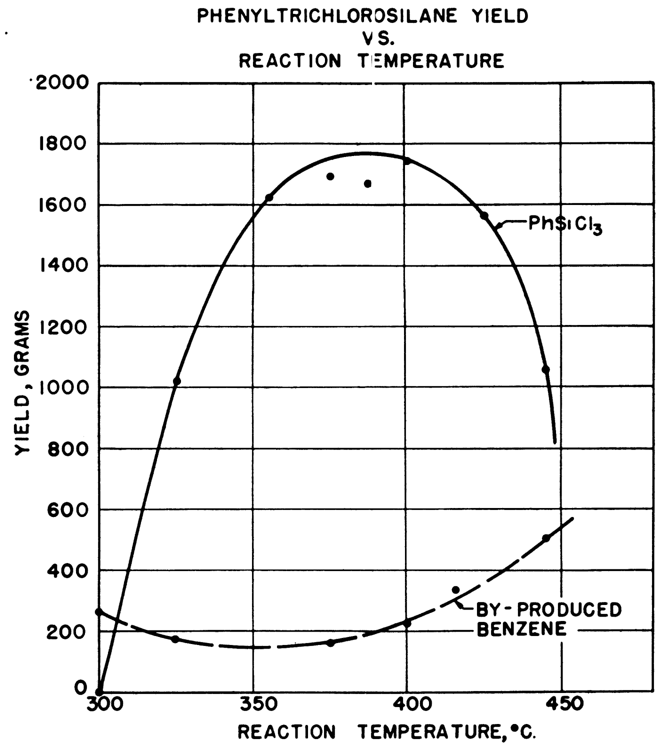


Figure 2. Thermal reaction of trichlorosilane with chlorobenzene

summarized in Table II and represented in the yield-temperature plot of Figure 2; 390°C. appears to be the optimum reaction temperature. At 300°C. essentially no phenyltrichlorosilane was formed in 16 hours; the only significant reaction occurring there was the reduction of chlorobenzene by trichlorosilane to give benzene. Above 400°C. the yield of phenyltrichlorosilane dropped off sharply and the formation of benzene increased markedly, as shown in the lower curve. Run 135 at 387°C. proved the most efficient of the series. Its 7.89 gram-mole yield of phenyltrichlorosilane represents 38.1% of the 20.7 gram-moles of trichlorosilane consumed and 65.8% of the 12 gram-moles of chlorobenzene charged; 2.7 gram-moles (22.5%) of the latter was reduced to benzene.

It might be concluded from the viewpoint of slightly lower threshold and lower optimum temperatures, that the chlorobenzene is more susceptible to reaction than

Table II. Reaction of Trichlorosilane with Chlorobenzene

Charge. 1352 grams (12 moles) C_6H_5Cl 14.4-liter autoclave
3257 grams (24 moles) $HSiCl_3$

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	$SiCl_4$, Grams	C_6H_6, Grams	C_6H_5Cl, Grams	$C_6H_5SiCl_3$, Grams	Residue, Grams
		16-hour runs						
FCB—236	300	4416	2060	301	264	1098	0	93
PB —133	325	4403	1054	1174	174	513	1027	140
102	355	4443	437	1985	30	112	1624	68
103	375	4518	236	1872	163	0	1696	128
135	387	4352	454	1778	212	0	1668	84
104	400	4554	291	1936	228	0	1745	86
134	416	4594	365	1861	336	0	1394	180
105	425	4473	349	1982	339	0	1565	85
136	445	4475	587	1817	504	0	1053	206
		6-hour run						
244	408	4452	285	2001	176	39	1721	190
		2-hour run						
165	423	4244	422	1740	197	89	1693	68

benzene. The process still is not more efficient with respect to the economically critical reagent—trichlorosilane—inasmuch as more silicon tetrachloride than the desired product is formed. This is inherent in the reaction because, for every molecule of trichlorosilane represented in silylation, one more is consumed by the hydrogen chloride formed. The ideal reaction is:

$$PhCl + 2\ HSiCl_3 \rightarrow PhSiCl_3 + SiCl_4 + H_2$$

It is accompanied by rearrangement of trichlorosilane as a side reaction which also generates silicon tetrachloride.

Two series of runs of 6- and 2-hour duration over the temperature range of 325° to 450°C. indicated incomplete reaction below 370°C. The 6-hour runs approached complete consumption of reagents and peak yields at about 410°C., the 2-hour runs at about 420°C. The peak run in each case is included in the table. The yields and efficiencies are close to those cited above for the 16-hour runs. Varying the mole ratio of trichlorosilane-chlorobenzene from 2:1 to 1:2 showed no effect upon yield or efficiency based upon the trichlorosilane.

In these runs, by-product phenyldichlorosilane was produced in variable amounts, but markedly less than in the benzene reactions. A composite of the distillation residues of a dozen runs at 400°C. was subjected to a further fractional distillation, from which small amounts of bis(trichlorosilyl)benzene (11.4% of tails), diphenyldichlorosilane (39.4%), and biphenyltrichlorosilane (15.3%) were isolated and identified (Table IX). A trace of chlorophenyltrichlorosilane was indicated.

Preparation of Tolyltrichlorosilane. Tolyltrichlorosilane was prepared in the same manner as phenyltrichlorosilane. Nine gram-moles each of toluene and trichlorosilane were heated in a 14.4-liter steel bomb for 16 hours at 420° to 440°C. Eighty-two per cent of the load weight was recovered and fractionated. This afforded 0.75 gram-mole of tolyltrichlorosilane (8.3% theoretical). Also isolated was 0.64 gram-mole of phenyltrichlorosilane.

In other preparations of this compound, halotoluenes were employed to take advantage of the somewhat lower temperatures that characterized the chlorobenzene reactions. Thus, in Table III are shown three runs of 12 to 13 hours' duration at 370° to 380°C. in a 2.4-liter steel bomb charged with 6 gram-moles of trichlorosilane and 3 gram-moles of the indicated halotoluene. In run 283, using chlorotoluene, the 38.5% yield (based on trichlorosilane consumed) is commensurate with the analogous phenyltrichlorosilane preparations. Reduction of aryl halide was less than in the chlorobenzene reaction (0.53 gram-mole of toluene found).

The reactions with the bromotoluenes were interesting, in that two compounds were produced in each run; the mole ratio of tolyltrichlorosilane to tolylbromodichlorosilane in each case is very nearly 2.0. This fits the probability calculation for a random distribution of halogen in a system containing six atoms of chlorine to one of

Table III. Reaction of Trichlorosilane with Aryl Halides

Charge. 3 moles aryl halide, 6 moles $HSiCl_3$ — 2.4-liter autoclave

Run	Aryl Halide	Reaction Time, Hr.	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	$SiCl_4$, Grams	Residue, Grams	Other Compounds	Wt., Grams
FCB—283	*p*-Chlorotoluene	12	375	1173	148	457	41	Chlorotoluene	51
								Toluene	49
								Tolyl $SiCl_3$	425
328	*o*-Bromotoluene	13	374	1272	131	375	17	$BrSiCl_3$	292
								Br_2SiCl_2 + toluene	275
								Tolyl $SiCl_3$	81
								Tolyl $SiBrCl_2$	51
335	*p*-Bromotoluene	12	369	1248	131	373	18	$BrSiCl_3$	235
								Br_2SiCl_2 + toluene	275
								Tolyl $SiCl_3$	107
								Tolyl $SiBrCl_2$	64
288	Chloroethylbenzene	12	375	1210	124	405	42	Chloroethylbenzene	132
								Ethylbenzene	70
								Ethylphenyl $SiCl_3$	409
289	Cumylchloride	12	375	1253	191	374	29	Cumylchloride	100
								Cumene	55
								Cumyl $SiCl_3$	432
358	2-Chlorobiphenyl	16	373	1316	185	479	26	Biphenyl	319
								m-Biphenyl-$SiCl_3$	176
								p-Biphenyl-$SiCl_3$	84
360	4-Chlorobiphenyl	14	374	1168	102	435	23	Biphenyl	329
								m-Biphenyl-$SiCl_3$	131
								p-Biphenyl-$SiCl_3$	57

bromine. The *p*-bromotoluene showed a higher yield than the ortho isomer (14.3 and 10.4%, respectively), but both are far less efficient than the chlorotoluene reaction. The low yields are reflected in large amounts of by-product tetrachlorosilane, bromotrichlorosilane (boiling point 80°C.), dibromodichlorosilane (boiling point 104.5°C.), and toluene. In each run, over 2 moles of the latter were formed by the easy reduction of the bromotoluene by trichlorosilane.

Preparation of Other Aryltrichlorosilanes. The adaptation of this process to the synthesis of substituted arylchlorosilanes in general is illustrated by the last four examples of Table III. These runs were of 12 to 16 hours' duration at 368° to 380°C. on a bomb charge of 3 gram-moles of aryl halide and 6 gram-moles of trichlorosilane.

The ethylphenyltrichlorosilane preparation (run 288) involved the use of a mixture of isomers of chloroethylbenzene. Product cuts, distilling over the range of 129° to 132°C. at 30 mm., amounted to 1.71 gram-moles (34.3% on trichlorosilane). The major amount, about 1 mole, was isolated over a narrow range, 130–30.5°C. at 30 mm. Ultimate analysis agreed well with theory as shown in Table IX; because of its relatively low boiling point, the compound is believed to be the meta derivative. The higher boiling product presumably containing the para isomer was not well resolved, but it, too, showed the expected ultimate analysis.

The cumyltrichlorosilane was made from a mixture of chlorocumene isomers. About 60% of the 1.7 gram-mole product distilled over the narrow range shown in Table IX. This cut, apparently the meta derivative, and other cuts up to 144°C. at 31 mm., presumably containing the para isomer, showed analyses in excellent agreement with theoretical. As was the case with chlorotoluene, both chlorocumene and chloroethylbenzene showed less reduction than chlorobenzene in reactions at comparable temperatures.

Biphenylyltrichlorosilanes were prepared from the *o*- and *p*-chlorobiphenyls as shown in the last two runs of Table III. The two isomers gave identical products, and in nearly the same ratios. The 2-chlorobiphenyl run gave a little better yield than the 4-chlorobiphenyl, but both gave less than 20% theoretical based on trichlorosilane. Each showed about 2.1 gram-moles of biphenyl from reduction of the aryl halide. The two biphenylyltrichlorosilane isomers were isolated as sharp cuts in fractional distillation. Both showed analytical data in good agreement with theoretical, and appropriate infrared absorptions for the isomer indicated. The designation of the para isomer is further supported by its higher boiling point and crystalline nature.

Preparation of Phenylmethyldichlorosilane. Benzene-Methyldichlorosilane Sys-

tem. That this general synthetic method is applicable to the reaction of methyldichlorosilane with aryl compounds is illustrated by the following study.

Three gram-moles each of benzene and methyldichlorosilane were heated together in a 2.4-liter bomb at 470° to 530°C. for 8 hours. Distillation of the material afforded a cut of 110 grams boiling in the range of 102° to 103°C. at 30 mm. while 2.2 gram-moles of benzene and 0.32 gram-mole of methyldichlorosilane were recovered. Considered as methylphenyldichlorosilane, this cut represents a yield of about 21% theoretical (based on methyldichlorosilane consumed). The high density (1.19) and chlorine content (39.3%) of the product compared with the theoretical (1.18 and 37.2%, respectively) for this compound, indicated that the methylphenyldichlorosilane was contaminated with a small amount of phenyltrichlorosilane whose boiling point is too close to afford a clean separation.

A similar experiment at 329° to 347°C. yielded no product. A series of four runs was made at a variety of closely controlled temperatures to determine the optimum. These runs employed 18 gram-moles each of benzene and methyldichlorosilane in a 14.4-liter steel bomb. They were held at a particular temperature for 16 hours. The data are summarized in Table IV, from which it is apparent that a maximum yield of

Table IV. Reactions with Methyldichlorosilane

$C_6H_6 + CH_3SiHCl_2$

Charge. 1402 grams (18 moles) C_6H_6; 2046 grams (17.78 moles) CH_3SiHCl_2 — 14.4-liter autoclave; 16-hr. reaction time

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	CH_3SiHCl_2, Grams	$SiCl_4$, Grams	CH_3SiCl_3, Grams	C_6H_6, Grams	$C_6H_5SiHCl_2$, Grams	$C_6H_5(CH_3)$-$SiCl_2$,[a] Grams	Residue, Grams
PB—121	355	3271	149	526	126	357	517	133	551	362
120	380	3244	208	325	0	506	691	237	550	364
119	405	3636	162	286	79	630	369	509	602	634
118	428	2976	124	177	74	416	780	200	562	541

$C_6H_5Cl + CH_3SiHCl_2$

Charge. 2031 grams (18.1 moles) C_6H_5Cl; 4055 grams (35.3 moles) CH_3SiHCl_2 — 14.4-liter autoclave; 16-hr. reaction time

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	CH_3SiHCl_2, Grams	$SiCl_4$, Grams	CH_3SiCl_3, Grams	C_6H_6, Grams	C_6H_5Cl Grams	$C_6H_5(CH_3)$-$SiCl_2$,[a] Grams	Residue, Grams
PB—128	355	5989	37	901		2330	524	1527[a]	107	289

[a] Contaminated with $C_6H_5SiCl_3$.

1010 grams of methylphenyldichlorosilane (33.2% theoretical) is obtained in the range of 400° to 410°C. The product yields in this system are generally equivalent or slightly inferior to those of the benzene-trichlorosilane system (compare with Figure 1) and follow the same trend with temperature. The product cut was contaminated with phenyltrichlorosilane, and considerable phenyldichlorosilane was isolated. The latter was probably formed from dichlorosilane arising from the thermal rearrangement of the methyldichlorosilane. This rearrangement is reflected also in significant quantities of trichlorosilane, silicon tetrachloride, and methyltrichlorosilane isolated in the distillations. Excessive amounts of high boiling residues remained after isolation of the product cuts. They average about sevenfold the amount of residue incidental to the preparation of phenyltrichlorosilane in the benzene-trichlorosilane system.

Chlorobenzene-Methyldichlorosilane System. In an orientation experiment, a mixture of 4 gram-moles of methyldichlorosilane with 2 of chlorobenzene was heated in a 2.4-liter bomb for 16 hours at 445° to 460°C. Distillation of the bomb product afforded a cut of 116 grams boiling at 114–15°C. at 50 mm., which showed a specific gravity (20°C./20°C.) of 1.200 and a chlorine analysis of 39.5%, both too high for pure methylphenyldichlorosilane. By calculation, the chlorine value indicated the presence of 15.7 mole % phenyltrichlorosilane to be present. This is confirmed by mole volume calculations from which a specific gravity of 1.204, in agreement with that found, is computed for a mixture of 84.3 mole % methylphenyldichlorosilane with 15.7 mole % phenyltrichlorosilane. The product yield was only about 16% theoretical based on consumed methyldichlorosilane. The low yield was reflected

in by-products, 2.04 gram-moles of methyltrichlorosilane and 0.12 gram-mole of dimethyldichlorosilane from thermal redistribution reaction of methyldichlorosilane. Of the 2 moles of chlorobenzene charged, 1.3 moles was reduced to benzene.

In one large run, 35.3 gram-moles of methyldichlorosilane and 18.1 gram-moles of chlorobenzene were heated together in a 14.4-liter steel bomb for 16 hours at 350° to 360°C. The data are presented at the bottom of Table IV. The product (8.0 moles) corresponds to a yield of 29.7% based upon consumed silane. Only a trace of trichlorosilane was produced, but 37% of the chlorobenzene charged (or 43% of the 15.5 gram-moles consumed) was reduced to benzene. It appears that methyldichlorosilane is a more powerful reducing agent than trichlorosilane (compare Table II).

Catalyzed Reactions

Preparation of Phenyltrichlorosilane. The preparation of arylchlorosilanes from hydrogen-containing chlorosilanes and the appropriate benzenoid compounds was successful, but accompanied by a number of disadvantages. Temperatures in the order of 400°C. were required. Operating pressures were consequently high (ranging up to 2000 p.s.i.). The yields of desired product were only fair, by-products were excessive, particularly those coming from thermal destruction of the starting chlorohydrosilane. The efficiencies were correspondingly low.

Benzene-Trichlorosilane-MX_3 System. To improve upon the process, catalyzed systems were investigated. The initial work embraced catalysts of the Friedel-Crafts type. Accordingly, a series of experiments was run with a variety of catalysts, each over a range of temperatures. All other variables were held constant. The reactants charged to the 14.4-liter steel bomb comprised 1402 grams of benzene and 2440 grams of trichlorosilane (18 gram-moles each). Catalyst amount was held in the order of 1 to 2% of total charge (safely above a determined minimum requirement). Reaction time was 16 hours. The data pertinent to this study are compiled in Table V. The temperatures of individual runs were held generally within ± 8°C. of the recorded figure. The pressures were autogenous, the maximum being recorded in each case. The reported results are based upon careful fractional distillations using a column of 20 theoretical plate rating. Discussion of the results will be facilitated by reference to Figure 3, which delineates the significant observations.

Aluminum Chloride Catalyst. The use of aluminum chloride promoted the reaction of benzene with trichlorosilane at lower temperatures than were operable without it. Whereas the uncatalyzed reaction showed only a trace of product at 345°C., the use of aluminum chloride afforded an apparent maximum of nearly 4.5 gram-moles at this temperature. A significant but diminishing yield was realized as the temperature was dropped to 305°C. Despite operability at lower temperature and consequently lower pressure, the ultimate yields of this catalyzed system were not improved over the uncatalyzed, nor was the by-product silicon tetrachloride suppressed. Large distillation residues appeared and considerable decomposition occurred during the distillation, attributable to cleavage catalyzed by aluminum chloride and its complexes in the pot residues. A preliminary flash distillation from the aluminum chloride afforded some relief; so did separation of the aluminum chloride as a eutectic with sodium chloride. However, neither offered a completely clean solution to the problem.

Boron Fluoride Catalyst. The preceding observations suggested a search for a more volatile catalyst or one whose complexes would be less destructive during distillation. The data on boron fluoride catalysis proved very promising. One minor, but practically important, difficulty appeared. While excellent yields of phenyltrichlorosilane were obtained, product isolation was complicated by the presence of phenyldichlorofluorosilane and phenylchlorodifluorosilane. For consideration of product yields, the mole equivalent weights of these compounds calculated as phenyltri-

Table V. Catalyzed Reaction of Trichlorosilane with Benzene

Charge. 1402 grams (18 moles) C_6H_6 14.4-liter autoclave
2440 grams (18 moles) $HSiCl_3$ 16-hr. reaction item

Run	Catalyst, Grams	Av. Temp., °C.	Max. Press., P.S.I.	Still Charge, Grams	$HSiCl_3$, Grams	$SiCl_4$, Grams	C_6H_6, Grams	$C_6H_5SiCl_3$, Grams	$C_6H_5SiCl_2F$, Grams	Residue, Grams	Product as $C_6H_5SiCl_3$, Grams	$C_6H_5SiCl_3$/$SiCl_4$ Wt. Ratio
PB—202	$AlCl_3$ 38	305	1020	3609	773	543	946	619		255	619	1.14
203	$AlCl_3$ 38	324	1250	3586	636	462	851	847		383	847	1.83
274	$AlCl_3$ 38	346	....	3364	418	597	928	943		41	943	1.58
275	$AlCl_3$ 38	364	....	2405	164	343	946	661		86	661	1.93
276	$AlCl_3$ 38	375	....	2853	271	559	807	932		248	932	1.67
306	$AlCl_3$ 39	400	1500	3345	281	539	691	927		705	927	1.72
290	BF_3 46	264	860	3358	298	374	565	1343	143	379	1498	4.00
291	BF_3 81	295	1020	3200	359	458	614	1054	128	480	1182	2.58
279	BF_3 64	305	1020	3444	289	514	644	1358	145	341	1515	2.95
292	BF_3 94	317	1100	3387	329	622	673	1024	100[a]	377	1222	1.96
280	BF_3 50	323	1150	3348	449	545	83	1043	81	297	1131	2.08
293	BF_3 39	329	1180	3420	399	533	631	1185	77	447	1268	2.37
281	BF_3 52	352	1400	3392	518	530	767	959	146	446	1117	2.09
294	BF_3 41	360	1400	3331	268	602	690	1304	67	196	1377	2.28
282	BF_3 113	375	1450	3297	259	668	731	854	214	272	1086	1.60
283	BF_3 47	375	1380	3456	331	585	705	1265	...	326	1265	2.16
304	BCl_3 79	226	420	3571	2001	97	1079	0		208	0	0
296	BCl_3 44	229	500	3405	1911	64	1146	0		168	0	0
297	BCl_3 40	251	600	3384	1552	111	1108	412		166	412	3.71
315	BCl_3 37	261	780	3440	890	254	826	1042		310	1042	4.10
316	BCl_3 50	275	880	3358	396	412	569	1452		426	1452	3.53
312	BCl_3 39	276	900	3400	450	389	585	1510		368	1510	3.88
298	BCl_3 40	278	840	3428	320	344	588	1583		303	1583	4.60
317	BCl_3 43	290	900	3405	321	421	746	1498		353	1498	3.56
284	BCl_3 90	299	980	3422	420	515	639	1357		416	1357	2.64
313	BCl_3 44	311	1100	3378	475	486	661	1360		380	1360	2.80
288	BCl_3 40	318	1230	3464	455	495	694	1218		564	1218	2.46
299	BCl_3 50	332	1010	3415	421	505	606	1415		380	1415	2.80
289	BCl_3 45	354	1240	3443	408	525	620	1435		315	1435	2.74
300	BCl_3 42	370	1400	3435	347	581	680	1131		377	1131	2.39
305	BCl_3 41	399	1500	3292	307	618	555	1069		586	1069	1.73

[a] Also 75 grams $C_6H_5SiClF_2$.

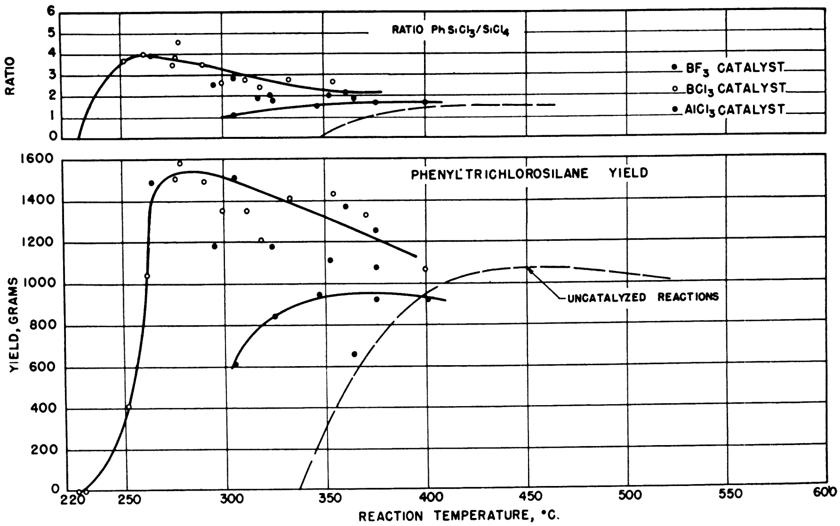


Figure 3. Catalyzed reaction of trichlorosilane with benzene

chlorosilane were included in the recorded product. Because the data on catalysis with boron fluoride were indistinguishable from those on boron chloride and because the latter must have been formed even in the present system by random halide rearrangement, this system is discussed in conjunction with the boron chloride experiments to follow.

Boron Chloride Catalyst. The data of Table V and their plots in Figure 3 show boron chloride (or boron fluoride) to be outstanding in catalysis of the reaction of benzene with trichlorosilane. The threshold temperature for the reaction is lowered to 240°C. The yield curve for the boron halide–catalyzed runs shows a maximum in the range of 265° to 280°C. The yields of phenyltrichlorosilane are significantly better than those obtained without catalyst or with aluminum chloride. Furthermore, production of silicon tetrachloride is suppressed, as is evident by studying the plot of phenyltrichlorosilane–silicon tetrachloride weight ratios. At optimum temperatures, these lie comfortably close to 4.0 for boron chloride catalysis as opposed to 1.8 with aluminum chloride or less than 1.5 without catalyst. In contrast to the isolable yields of phenyldichlorosilane noted in the uncatalyzed experiments, the boron halide–catalyzed runs showed only a little of this by-product. It was detected in the bomb product via infrared spectroscopy.

By reference to Table V, it is seen that the boron halide–catalyzed runs are characterized by higher distillation residues, about threefold the amounts observed in uncatalyzed operation. However, these residues contain useful by-products and their silylation values should be included in any assay of the reaction efficacy. For example, when the distillation residue of six runs (288, 296–7, 304–5, 312) were combined to afford enough still load for a further careful fractional distillation, the following were isolated: phenyltrichlorosilane (8.9% of still load); diphenyldichlorosilane (14.0%); hexachlorodisilylbenzene (14.9%); phenylpentachlorodisilylbenzene (9.3%); remainder, a black tar incapable of further resolution. Identification of these compounds, two of them isolated as both liquid and crystalline isomers, and their characterizations will be found in Table IX.

The boron-catalyzed system is markedly superior to the uncatalyzed. For comparison, evaluation of the best boron-catalyzed run (312) is summarized in the following table.

Boron-Catalyzed Reaction

	Actual	Potential
Phenyltrichlorosilane yield, %		
Trichlorosilane basis	49.8	58.0
Benzene basis	69.6	87.0
Silylation yield, %		
Trichlorosilane basis	56.6	65.8
Benzene basis	79.2	98.7
Silicon balance, gram-atoms	14.38	17.21
Phenyl balance, gram-moles	15.56	17.60

The actual results in the first column represent products isolated from the still load. The potential results are based upon a correction of the distillation data to account for mechanical losses, particularly in discharging the bomb. The phenyltrichlorosilane yields are based upon reagents consumed; the silylation yields relate the number of Si—C bonds established (in product and identified by-products) to the mole-reagent consumption; the silicon balance is a total gram-atom count in all identifiable compounds, remembering that each gram-mole of silicon tetrachloride represents 1.33 gram-atoms of silicon; the phenyl balance counts all phenyl groups identifiable.

Because in these systems lower temperatures were required than in the uncatalyzed systems, the operating pressures were lower. They varied consistently with temperature from about 400 p.s.i. at 225°C. to 1500 p.s.i. at 400°C.

Preparation of Aryltrichlorosilanes. Toluene-Trichlorosilane–Boron Chloride System. Compared with benzene, the generally greater reactivity of toluene under onium ion attack made it a point of interest in the synthesis of aryltrichlorosilanes. Accordingly, the reaction of toluene with trichlorosilane was studied in exactly the same manner as for benzene. The pertinent data are condensed in Table VI and the significant trends plotted in the two curves of Figure 4.

Table VI. Catalyzed Reaction of Trichlorosilane with Toluene

Charge. 1656 grams (18 moles) $C_6H_5CH_3$; 2440 grams (18 moles) $HSiCl_3$; BCl_3: 1.0–1.3% of charge. 14.4-liter autoclave; 16-hr. reaction time

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	$SiCl_4$, Grams	$MeSiCl_3$, Grams	C_6H_6, Grams	$C_6H_5CH_3$, Grams	$C_6H_5SiCl_3$, Grams	$CH_3C_6H_4SiCl_3$, Grams	Residue, Grams
PB—361	222	3880	2251	0	0	0	1384	0	0	180
343	242	3799	966	232	0	0	843	0	1475	232
344	261	3869	438	420	0	0	689	0	1772	443
345	286	3999	587	505	39	28	648	33	1534	578
301	300	3870	433	459	28	35	776	80	1376	590
346	312	3986	374	565	89	34	714	104	1330	686
347	351	3915	279	638	157	52	701	135	1147	776

The threshold temperature for the reaction lies between 222° and 242°C., some 20°C. lower than for the benzene reactions. The yield of tolyltrichlorosilane approaches a maximum near 260°C., also lower than for benzene reactions. At higher temperatures, the yields become progressively lower because of the thermal rearrangement of trichlorosilane, reflected in progressively greater amounts of silicon tetrachloride. At temperatures above 285°C., phenyltrichlorosilane, benzene, and methyltrichlorosilane make their appearance, possibly as scission products of an intermediate ortho-adduct discussed in the theoretical section below.

The maximum yield of tolyltrichlorosilane in this series amounted to 7.86 gram-moles or 53.2% theoretical, based upon unrecovered trichlorosilane. However, the highest product–silicon tetrachloride ratio is observed in run 343, nearest the threshold temperature. Here the reaction was far short of completion in the 16-hour reaction time at 242°C., but it proved the most efficient of the series since the 6.54 gram-mole yield represents 60.4% theoretical based upon consumed trichlorosilane.

Mesitylene-Trichlorosilane–Boron Chloride System. It was interesting to study this reaction, inasmuch as scission of an ortho-adduct (β-elimination) affords a reasonable explanation for formation of some phenyl compounds in the toluene runs

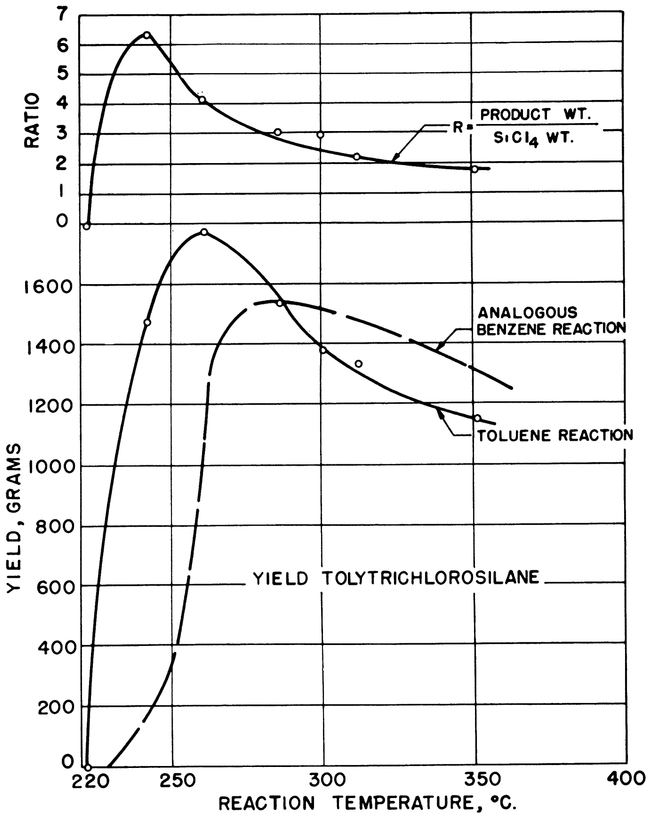


Figure 4. Catalyzed reaction of trichlorosilane with toluene

above. With mesitylene the attacking group can only go ortho to a methyl group on the benzene ring. A mixture of 2.08 gram-moles of mesitylene and 4.0 gram-moles of trichlorosilane was bombed with 0.08 gram-mole of boron trichloride in a 2.4-liter unit, for 15 hours at 308° to 316°C. While the temperature was accidentally higher than intended, the reaction was sluggish and only 0.34 gram-mole of mesityltrichlorosilane was obtained by fractional distillation. It was isolated as a cut at 142–2.5°C. at 30 mm. and was identified by proper analytical data as shown in Table IX. It is significant that 0.34 gram-mole of xylene was recovered in low-boiling forecuts. An 86-gram cut boiling over the range of 127° to 134°C. at 30 mm. was identified as xylyltrichlorosilane. Most significantly, 0.42 gram-mole of methyltrichlorosilane was found. It is to be expected in the event of ortho elimination, which must be the reason for the observed xylene and its derivative; the amount is large compared with toluene runs, as expected, because mesitylene offers only ortho sites for reaction.

Biphenyl-Trichlorosilane–Boron Chloride System. Biphenylyltrichlorosilane was made by heating a mixture of 18 gram-moles each of biphenyl and trichlorosilane containing 0.5 gram-mole of boron trichloride in a 14.4-liter bomb for 16 hours at 265° to 270°C. The bomb was incompletely discharged, but 4648 grams of product gave on distillation 2.21 gram-moles of *m*-biphenylyltrichlorosilane and 3.97 gram-moles of the crystalline para isomer (6.18 gram-mole total). Allowing for 2.16 gram-moles of recovered trichlorosilane, the yield is calculated to be conservatively 39.0% theoretical.

Phenyltrichlorosilane-Trichlorosilane–Boron Chloride System. Phenyltrichloro-

Table VII. Catalyzed Reaction of Methyldichlorosilane with Benzene

Charge. 1402 grams (18 moles) C_6H_6 14.4-liter autoclave
2070 grams (18 moles) CH_3SiHCl_2 16-hr. reaction time
BCl_3: 1.0–1.3% of charge

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	CH_3SiHCl_2, Grams	CH_3SiCl_3, Grams	$(CH_3)_2SiCl_2$, Grams	C_6H_6, Grams	$C_6H_5SiCl_3$, Grams	$C_6H_5(CH_3)SiCl_2$, Grams	Residue, Grams
PB—395	144	3343	0	1815	0	0	1295	0	0	199
413	151	2822	0	1179	——129——		888	0	299	146
394	160	3332	0	1299	95	59	1044	0	427	175
393	182	3265	60	664	198	59	947	38	771	288
386	203	3268	0	615	263	34	819	39	1035	381
385	241	3242	50	250	458	57	677	25	761	789
384	274	3221	51	187	435	94	698	106	289	1136
357	302	2854	93	227	307	151	640	210	139	1187

Table VIII. Catalyzed Reaction of Methyldichlorosilane with Toluene

Charge. 2070 grams (18 moles) CH_3SiHCl_2 14.4-liter autoclave
1656 grams (18 moles) $C_6H_5CH_3$ 16-hr. reaction time
BCl_3: 0.7–1.0% of charge

Run	Av. Temp., °C.	Still Charge, Grams	$HSiCl_3$, Grams	CH_3SiHCl_2, Grams	CH_3SiCl_3, Grams	$(CH_3)_2SiCl_2$, Grams	$C_6H_5CH_3$, Grams	$CH_3C_6H_4SiCl_3$, Grams	$CH_3C_6H_4(CH_3)SiCl_2$, Grams	Residue, Grams
PB—412	150	3566	0	1828	79	0	1469	0	0	161
398	169	3455	0	947	169	88	1251	46	380	333
418	177	3427	0	510	374	198	1051	42	731	316
383	186	3574	27	901	——291——		1093	79	873	182
397	206	3495	0	403	329	189	915	62	1003	430
366	241	3511	141	234	346	207	932	38	774	579
367	250	3519	85	187	341	309	986	40	662	587

silane (3810 grams), trichlorosilane (2440 grams), and boron chloride (64 grams) were bombed at 290° to 310°C. for 16 hours. The 5917 grams of material discharged from the reactor contained unreacted trichlorosilane (940 grams), phenyltrichlorosilane (1354 grams), by-product benzene (57 grams), and tetrachlorosilane (1132 grams).

In addition, the following compounds boiling above phenyltrichlorosilane were isolated:

	Grams
$(C_6H_5)_2SiCl_2$	80
m-$Cl_3SiC_6H_4SiCl_3$	476
p-$Cl_3SiC_6H_4SiCl_3$	141
$C_6H_5SiCl_2C_6H_4SiCl_3$	356
$Cl_3SiC_6H_4SiCl_2C_6H_4SiCl_3$	73

Five hundred and twenty grams of higher boiling material remained as still residue. The first four of the compounds were found in the still residues of boron chloride–catalyzed benzene-trichlorosilane reaction products. The last was probably there also, but in amount too small for isolation. The four new compounds are characterized in Table IX.

Preparation of Arylmethyldichlorosilanes. That the method just described for the silylation of benzenoid compounds by trichlorosilane may be extended more generally to other chlorohydrosilanes, was established by the following work. Procedures were identical with those of the foregoing experiments employing boron chloride as a catalyst.

Benzene-Methyldichlorosilane–Boron Chloride System. A series of runs was made in the 14.4-liter bomb using 18 gram-moles each of benzene and methyldichlorosilane with 1.0 to 1.5% boron chloride on total load weight. The runs were of 16 hours' duration and covered a wide range of reaction temperatures. Pressures ranged from 150 p.s.i. at 150°C. to 1300 p.s.i. at 300°C. Table VII summarizes the data essential for discussion. Reaction of methyldichlorosilane with benzene commences at a much lower temperature (145° to 151°C.) than the corresponding trichlorosilane reaction with either benzene or toluene, but the threshold is much less sharply defined (see Figure 5). With increase in temperature, the yield of methylphenyldichlorosilane increases to a maximum at about 203°C., then falls off at higher temperatures as redistribution reactions between the desired product and the initial methyldichlorosilane yield progressively more trichlorosilane, phenyltrichlorosilane, methyltrichlorosilane, and dimethyldichlorosilane. Extraordinarily high residues were observed at temperatures above 240°C. The best attempt at plotting a product–by-product ratio would relate the sum of the two phenylsilanes (both useful silyation products) to the sum of the two methylsilanes. As plotted against temperature in Figure 5, the curve seems to peak at about 203°C., where the maximum yield also occurs. The 5.60 gram-mole product represents a yield of 44.3% theoretical when allowance is made for recovery of 615 grams (5.35 gram-moles) of methyldichlorosilane.

Toluene-Methyldichlorosilane–Boron Chloride System. The reaction of toluene with methyldichlorosilane was almost identical in character to the foregoing benzene reaction. The essential data are condensed in Table VIII, and plotted in Figure 5 along with corresponding data on the benzene reaction. The two sets of data are hardly distinguishable. The threshold temperature lies in the range of 150°C., but is not sharply defined. The yield rises with temperature to a maximum of 4.9 gram-moles in the vicinity of 206°C. However, the best product–by-product ratio appears in the vicinity of 186°C. and, indeed, the reaction efficiency was best at this temperature (run 383). Here, the tolylmethyldichlorosilane yield was 4.26 gram-moles; allowing for 901 grams (7.84 gram-moles) of recovered methyldichlorosilane, the yield is calculated to be 41.9% theoretical. If the useful tolyltrichlorosilane be included in the product, the silylation yield becomes 45.4% theoretical. These figures are conservative in the face of some 4% handling losses.

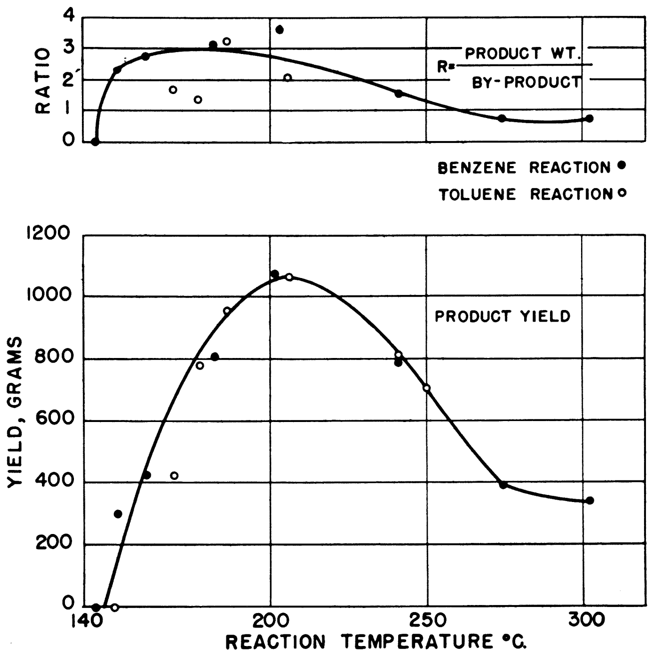


Figure 5. Catalyzed reaction of methyldichlorosilane with benzene and toluene

New Compounds

Many of the products synthesized by this direct process are well known in the field of organosilicon chemistry. Many others reported here are less common or

Table IX. New Compounds

Compound	Boiling Point, °C./30 Mm. Pressure	Sp.Gr. 20°/20°	Analyses, Found, % C	Found, % Si	Found, % Halide	Theoretical, % C	Theoretical, % Si	Theoretical, % Halide
m-$CH_3C_6H_4SiCl_3$[f]	118	1.279	37.4	12.8	47.0	37.2	12.4	47.2
m-$CH_3C_6H_4SiCl_3$[g]	116–119	....	...	12.6	47.4	37.2	12.4	47.2
m-$CH_3C_6H_4SiCl_3$[h]	116–119	1.288	37.6	12.6	49.0	37.2	12.4	47.2
m-$CH_3C_6H_4SiBrCl_2$[g]	131–134	....	...	10.4	39.7[a]	31.1	10.4	39.4[a]
m-$CH_3C_6H_4SiBrCl_2$[h]	131–134	....	32.0	10.6	40.8[a]	31.1	10.4	39.4[a]
m-$CH_3C_6H_4(CH_3)SiCl_2$	117–118	1.158	45.9	13.7	35.4	46.8	13.7	34.6
m-$C_2H_5C_6H_4SiCl_3$	130–130.5	1.245	40.7	11.8	44.9	40.1	11.7	44.4
m-$(CH_3)_2CHC_6H_4SiCl_3$	135-136	1.228	42.8	10.7	42.4	42.6	11.0	42.0
2,4,6-$(CH_3)_3C_6H_2SiCl_3$	142–142.5	1.217	42.2	10.6	41.2	42.6	11.0	42.0
$C_6H_5SiBr_3$	94–99[b]	....	25.7	7.5	66.0	24.5[c]	7.7[c]	66.1[c]
$C_6H_5SiClF_2$	130–135[d]	....	...	...	...	...	...	...
$C_6H_5SiCl_2F$	163–166[d]	....	...	...	36.3[k]	36.9	14.4	36.4[k]
m-$C_6H_5C_6H_4SiCl_3$[i]	203	1.307	...	9.9	37.1	50.1	9.7	37.1
m-$C_6H_5C_6H_4SiCl_3$[j]	203–203.5	1.306	...	10.1	37.2	50.1	9.7	37.1
p-$C_6H_5C_6H_4SiCl_3$[i]	209–211.5	Crystalline	...	10.1	37.4	50.1	9.7	37.1
p-$C_6H_5C_6H_4SiCl_3$[j]	209–209.5	Crystalline	...	10.3	37.1	50.1	9.7	37.1
m-$Cl_3SiC_6H_4SiCl_3$	161–161.5	1.497	21.0	16.2	62.5	20.8	16.5	61.8
p-$Cl_3SiC_6H_4SiCl_3$	168	Crystalline	21.2	16.6	64.2	20.8	16.5	61.8
$C_6H_5SiCl_2C_6H_4SiCl_3$	225–226.5	1.386	38.3	14.8	46.2	37.2	14.5	46.0
$Cl_3SiC_6H_4SiCl_2C_6H_4SiCl_3$	211–212[e]	1.49	28.7	16.4	54.0	27.7	16.1	54.6

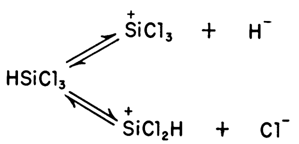
[a] Halide computed as chloride.
[b] Boiling point at 2.3–2.9-mm. pressure.
[c] Theoretical analysis with 6% biphenyl contamination.
[d] Boiling point at atm. pressure.
[e] Boiling point at 5-mm. pressure.
[f] Derived from *p*-chlorotoluene.
[g] Derived from *o*-bromotoluene.
[h] Derived from *p*-bromotoluene.
[i] Derived from 2-chlorobiphenyl.
[j] Derived from 4-chlorobiphenyl.
[k] % chlorine.

entirely new. For the sake of brevity and organization of the discussion it seemed wise to gather all the new compounds into one table for characterization and support of structure. Accordingly, Table IX shows the compounds isolated, their physical properties, and ultimate chemical analyses compared with the theoretical values. For isomer identification, infrared absorption spectra were obtained on several of the listed compounds and compared with the curves of Clark, Gordon, Young, and Hunter (*6*), who studied several species of ring-substituted phenylsilanes. They showed that isomer distinction could be viewed in the 5- to 6-micron region, but was particularly resolvable at longer wave lengths where ortho, meta, and para isomers were distinguished by absorption bands at 13 to 13.5, 12.5 to 13, and 12 to 12.5 microns, respectively. In this manner, the whole sample of tolyltrichlorosilane obtained by the boron-catalyzed synthesis was shown to be an equal mixture of meta and para isomers with a trace of ortho possibly present. The low boiling plateau in the table is undoubtedly the *m*-tolyltrichlorosilane.

For the biphenylyltrichlorosilanes and the bis(trichlorosilyl)benzenes, which were sharply cut in their distillation, the liquid fractions in both cases were pure meta isomers while the crystalline compounds were pure para isomers.

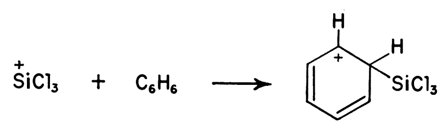
Theoretical Considerations

An ionic mechanism might best explain the formation of the products found in this work. This would first entail thermal dissociation of trichlorosilane, for example, to give siliconium ions capable of addition to the aromatic nucleus as indicated:



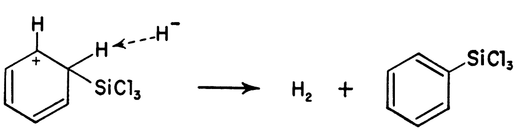
(1)

(2)



(3)

In classical manner, the imposition of the anion upon the latter, elimination of a neutral molecule, and redistribution of electrons on the ring should afford the observed products:



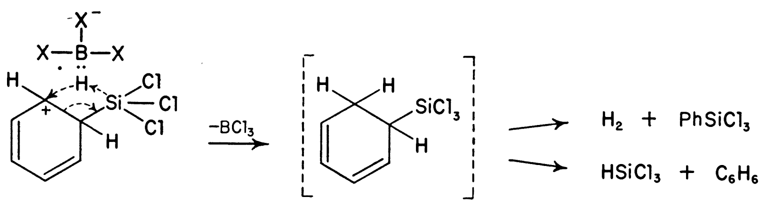
(4)

Similar disposition of the ions of (2) would afford the observed phenyldichlorosilane; the by-product hydrogen chloride in this case would be consumed by trichlorosilane to give hydrogen and silicon tetrachloride observed in the reactions or, by crossover of ions in 1 and 2, the Cl^- may have been scavenged by a $Cl_3\overset{+}{Si}$ leaving the hydranion to complete its task in the manner of 4. In the thermal runs the mole yields of phenyltrichlorosilane and phenyldichlorosilane are in the average ratio of 5.0 to 1, respectively; correspondence may be presumed for the source siliconium ions. Interestingly, mass spectroscopy shows trichlorosilane to cleave into $\overset{+}{Si}Cl_3$ and $H\overset{+}{Si}Cl_2$ fragments in an abundance ratio of 4.93 to 1, respectively.

The catalyzed reactions reported in this work were observed to require less

drastic thermal conditions than those without catalyst. This is compatible with classical theory on the basis that boron chloride, for example, may coordinate with the anions of Equations 1 and 2 to form somewhat more stable complex ions, $(Cl:BCl_3)^-$ and $(H:BCl_3)^-$, respectively, thus pulling 1 and 2 to the right and increasing the probability of adduct 3. Methyl substitution in the chlorosilane should also be conducive toward this end because of increased positive charge on the silicon. The lower temperatures required for reaction of methyldichlorosilane support this view. In this mechanism there is no need to presume any great ion separation.

The classical interpretation outlined above accounts satisfactorily for the main products obtained. However, it does not predict some of the by-products observed nor explain the absence of other compounds anticipated—e.g., ortho isomers. Some modification seems necessary, and the following concept is offered for consideration. Instead of abstracting a proton as postulated above, the anion might approach the carbonium site of Equation 3 to give a neutral molecule. The resultant conjugated cyclohexadiene derivative would be highly unstable and, seeking resonance stability, would immediately undergo ortho elimination, yielding the observed products of regenerating the starting materials:



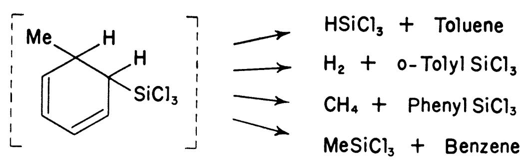
(5)

The actual existence of a cyclohexadiene derivative is not absolutely essential to this interpretation, but a tendency toward such an intermediate state may be presumed on the basis of a concerted interaction involving:

The known electrophilic character of the central silicon atom.
Polarization of the aromatic nucleus with an attraction of its induced partial negative charge toward the silicon.
Coordination of boron halide with potential anion from the silicon and withdrawal of it sufficiently to permit imposition of the anion, simple or complex, upon the carbonium site of the aromatic ring.

The sequence is illustrated with hydranion migration in Equation 5. Potential homopolar bonding of H—C, tending toward the postulated cyclohexadiene intermediate, is considerably more tenable than analogous treatment of a chlorine anion. The heteropolar character of the potential Cl—C bond would be more likely to encourage beta-cleavage of the silyl group from the carbonium ion as has been described in the case of β-haloalkylsilanes (*14*). It is significant that in the present work no haloaryl silicon compounds have been detected among the by products from the reactions of aryl hydrocarbons with halohydrosilanes.

The concept of mechanism outlined above is helpful in explaining many observations relating to this work, among them the matter of isomers obtained. In common with all syntheses in which disubstituted benzenes were obtained, the reactions of toluene with halohydrosilanes showed little or no indication of ortho compounds. This is remarkable in the face of high yields of *o*-nitrotoluene from the nitration (nitronium attack) of toluene (*7*). Steric factors, attributable to the large size of the silyl group, can offer only a partial explanation. Indeed, while the major attack was meta and para, ortho-adduction must have occurred to explain the byproducts observed in the tolyltrichlorosilane preparations, particularly where forced by higher temperatures. If we examine the possible ortho adduct of toluene and trichlorosilane in the convenience of Reaction 5, the hypothetical intermediate would have 4 modes of scission to regain benzenoid stability.



(6)

The first line of scission would merely regenerate the starting materials. The second would yield hydrogen, in common with scission of other adducts, and *o*-tolyltrichlorosilane which was indicated only in trace amount too small for identification; the remaining two modes of cleavage should yield methane, found in the vent gases from the bomb, and the other three by-products indicated, all of which were identified among the forecuts in product distillation.

The reaction with mesitylene was particularly illuminating, for here the trichlorosiliconium ion could attack only positions ortho to a methyl group. Mesityltrichlorosilane was obtained as reported, but was exceeded by the molar amounts of methyltrichlorosilane and xylene plus xylyltrichlorosilane, as might be expected by reasoning analogous to that for the toluene reaction above.

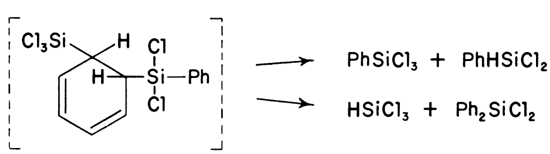
Similar considerations can be applied to explain the absence of ortho isomers among the polysubstitution compounds produced in the preparation of phenyltrichlorosilane by the boron chloride–catalyzed reaction of trichlorosilane and benzene:

$$HSiCl_3 + C_6H_6 \nearrow PhSiCl_3 \xrightarrow{HSiCl_3} Cl_3SiC_6H_4SiCl_3$$

$$HSiCl_3 + C_6H_6 \searrow PhSiCl_2H \xrightarrow{C_6H_6} Ph_2SiCl_2 \xrightarrow{HSiCl_3} PhSiCl_2C_6H_4SiCl_3 \qquad (7)$$

Clean cuts of *m*- and *p*-bis(trichlorosilyl)benzenes and their monophenyl derivatives were obtained in copious quantities, but no ortho isomer was detected. From attempts to build such a structure with scaled atomic models, an ortho isomer seems almost impossible. An approach to the hypothetical ortho adduct of trichlorosilane to phenyltrichlorosilane could be realized only with the bulky trichlorosilyl groups in the trans-configuration. Cleavage of this in either of the two likely ways—cis—could yield only trichlorosilane and phenyltrichlorosilane. That no hexachlorodisilane has been detected in these experiments both supports the trans configuration and argues against trans elimination.

An interesting case for the ortho elimination concept resides in the reaction of trichlorosilane with phenyltrichlorosilane. Here the major product, bis(trichlorosilyl)-benzene, is of now obvious origin; the by-products, diphenyldichlorosilane, phenyl-(trichlorosilylphenyl)dichlorosilane, and bis(trichlorosilylphenyl)dichlorosilane arrive by more devious route. Phenyldichlorosilane, the key to a most likely explanation, may be formed by redistribution (exchange between hydranion from trichlorosilane and chloride ion from phenyltrichlorosilane). If the phenyldichlorosilane now reacts with phenyltrichlorosilane in the meta or para positions as in Reaction 4 or 5, the observed phenyl(trichlorosilylphenyl)dichlorosilane isomers should result. But, if the attack be ortho, the theory of Reaction 6 can be applied here with the limitation that the silyl groups on adjacent carbons be of trans-configuration:



(8)

The first elimination shown would merely regenerate the initial compounds; the second accounts nicely for the diphenyldichlorosilane observed. If the same sequence of reactions occur starting with bis(trichlorosilyl)benzene instead of phenyltrichlorosilane, bis(trichlorosilylphenyl)dichlorosilane should emerge as was found. Thus, these theoretical considerations adequately account for all products observed in this system.

The proposed reaction mechanism will be considered further in two papers dealing with the reaction of chlorohydrosilanes with naphthalene and aryl halides.

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Formation of Alkyl and Aryl Titanium-Carbon Bond Compounds

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The first compound synthesized and isolated, containing a titanium-carbon bond was phenyltitanium triisopropoxide. Much information was accumulated related to the preparation and properties of organotitanium compounds of the type R_nTiX_{4-n}, where R could be alkyl or aryl groups and X could be alkoxy groups or halogen. The organotitanium compounds can exist at various valence levels. Compounds of the type R_nTiX_m can exist when the sum of n and m is 2 or 3. These materials, although more stable than quadrivalent organotitanium compounds, exhibit some thermal instability and act as catalysts for polymerization. Reduction of titanium compounds by organometallic reagents takes place through the intermediate formation of an organotitanium compound. Reduction proceeds only to the extent of giving a mixture of bi- and trivalent compounds even in the presence of excess Grignard reagent. Reaction of the lower valent titanium compounds with the solvent may account for this.

Alkyl and aryl organometallic compounds containing direct carbon to titanium bonds are discussed. These carbon-metal bonds are of at least partial covalent character. New work is described which further elucidates the nature of the organotitanium compounds formed on reaction of organometallic reagents with titanium esters or chlorides at varying molar ratios. Conclusions or proposed structures are based upon diagnostic tests and chemical analyses similar to those by Herman and Nelson (*8*).

Although most of the compounds described are diffcult to handle and even more difficult to isolate in purified state, they are increasingly important as catalysts in heterogeneous polymerization. This field has grown rapidly since Ziegler's announcement (*18*) of the low pressure polymerization of ethylene by means of catalysts formed by the interaction of organometallic reagents, such as organoaluminum compounds, with various derivatives of titanium.

The initial attempt to prepare a stable and isolatable organotitanium compound was made in 1861 by Cahours (*3*). Many further attempts were also unsuccessful (*1, 2, 4, 7, 10–14, 16*). Under some circumstances, organotitanium products of a transitory nature may have been formed in solution, especially in the reactions of titanium

salts with various organometallic reagents (*7, 13*). A successful synthesis was reported in 1952 and 1953 by Herman and Nelson (*8*). The isolation of phenyltitanium triisopropoxide was described, and compounds of the type R_nTiX_{4-n} were discussed. Summers and Uloth (*17*) described an unusual series of compounds of the class $(C_5H_5)_2TiR_2$, where R is phenyl, *p*-tolyl, and *p*-dimethylaminophenyl. These materials possessed an unusual stability towards hydrolysis when compared to the simpler organotitanium compounds. This is attributed to the sandwich structure of the two cyclopentadiene rings. Friedlander and Oita (*6*) described the reaction products of alkyl lithium compounds and titanium tetrachloride at varying molar ratios and obtained evidence pointing towards transient titanium-carbon bonds. Diagnostic methods employed were similar to those described previously (*8*). These materials were active catalysts for the polymerization of ethylene.

Previous attempts to form R_nTiX_{4-n} compounds were unsuccessful, because the conditions selected for reaction were too stringent. Therefore, the initial reaction studied was one involving equimolar quantities of phenylmagnesium bromide and butyl titanate in ether at about 8°C. Evidence indicated that a phenyl-titanium bond of moderate stability had been formed *in situ*. The solution gave a slowly developing but eventually strong color test with Michler's ketone. Because Grignard reagents exhibit a very rapid positive test, it was assumed that phenylmagnesium bromide was no longer present and that a new organometallic compound—i.e., an organotitanium compound of lesser activity—had been formed. Substantiating this, carbonation of a phenylmagnesium bromide yielded 70 to 90% benzoic acid, and carbonation of the Grignard-titanate reaction mixture yielded only 0 to 2% benzoic acid. High yields of benzoic acid would be expected if there was no reaction of the Grignard reagent. Oxidation of the reaction mixture resulted in 20 to 25% yields of phenol along with some biphenyl and benzene. These results are identical to what is ordinarily obtained on oxidation of phenylmagnesium bromide. As the Grignard reagent is no longer present, these oxidation products must be attributed to a new type of organometallic compound. The authors concluded that this compound was a phenyltitanium compound formed according to Equation 1.

$$C_6H_5MgBr + (C_4H_9O)_4Ti \rightarrow C_6H_5Ti(OC_4H_9)_3 + C_4H_9OMgBr \quad (1)$$

The oxidation and hydrolysis reactions are shown in Equations 2 and 3.

$$C_6H_5Ti(OC_4H_9)_3 + \tfrac{1}{2}O_2 \rightarrow C_6H_5OTi(OC_4H_9)_3 \quad (2a)$$

$$C_6H_5OTi(OC_4H_9)_3 + H_2O \rightarrow C_6H_5OH + TiO_2 \text{ hydrate} + 3C_4H_9OH \quad (2b)$$

$$C_6H_5Ti(OC_4H_9)_3 + H_2O \rightarrow C_6H_6 + TiO_2 \text{ hydrate} + 3C_4H_7OH \quad (3)$$

Equation 2 has been substantiated by infrared evidence.

In the Grignard reagent–butyl titanate reaction mixture, reduced titanium compounds are formed gradually on storage at room temperature and inert atmosphere (Figure 1).

This decomposition will be discussed later, but two points should be emphasized here. (1) There is essentially no formation of reduced titanium immediately after completing the addition of Grignard reagent to the titanate. (2) At this point, the Grignard reagent had reacted completely to form organotitanium compounds. Therefore, the ensuing formation of lower valent titanium compounds is not attributed to a direct reducing action of the Grignard reagent but to a homolytic cleavage of the carbon-metal bond, as in Equation 4.

$$C_6H_5Ti\lessgtr \longrightarrow C_6H_5\cdot \quad \gtrless Ti\cdot \quad (4)$$

The formation of free phenyl radicals and lower valent titanium compounds containing odd electrons is postulated. The decomposition is believed to be unimolecular rather than bimolecular, because in bimolecular coupling reactions biphenyl is obtained

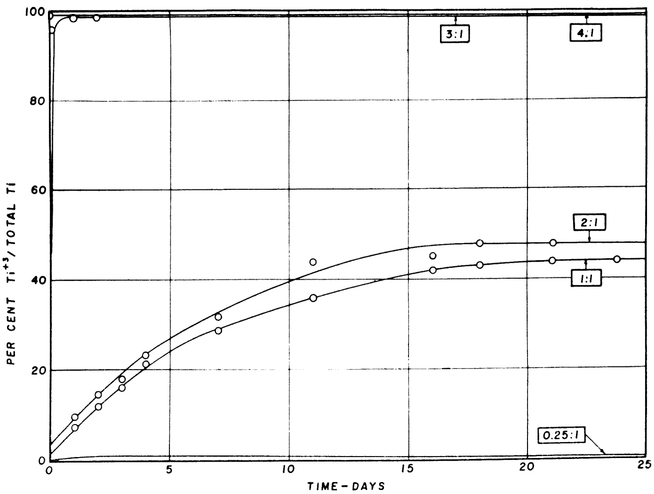


Figure 1. Decomposition rates of phenylmagnesium bromide and butyltitanate

1 to 1 to 4 to 1 molar ratios

in high yields (*5*). In the present instance, typical decomposition products are 33 to 34% benzene, 25 to 37% biphenyl, and up to 15% of higher aromatic hydrocarbons. The most striking evidence for such a thermal cleavage of the titanium-carbon bond is the ability of the reaction fragments to catalyze the polymerization of vinyl monomers.

The actual isolation of a phenyltitanium compound from these reaction mixtures was achieved by the reaction of phenyllithium with isopropyl titanate at 8° to 15°C. A transient orange color was produced which was followed by the deposition of well-formed white crystals analyzing as $C_6H_5Ti(OC_3H_7)_3 \cdot LiOC_3H_7 \cdot LiBr \cdot (C_2H_5)_2O$. Phenyltitanium triisopropoxide was isolated from this complex by reaction with titanium tetrachloride or aluminum chloride. It was obtained as a white crystalline substance, melting point 88° to 90°C., which was stable on storage at 10°C. Rapid decomposition to titanous products took place on heating at 100° to 120°C. The product exhibited all of the reactions previously described in the *in situ* formation of phenyltitanium compounds. Therefore, the diagnostic methods previously described are reliable, and this approach may be used with reasonable confidence in demonstrating the existence of organotitanium bonds in reaction mixtures of organometallic reagents with titanium derivatives.

The stabilities of titanium-carbon bonds in compounds of the general form R_nTiX_{4-n} were studied. R groups were varied from alkyl to aryl, attempts were made to link more than one R group to the titanium atom, and X was varied from alkoxide to halide. The general conclusion was that titanium-carbon bonds of variable stability existed in all cases. With variation in the R group, stability increased: butyl $<$ methyl $<$ acetylenyl $<$ *p*-anisyl $<$ phenyl $<$ 2-naphthyl $<$ indenyl. The indenyl group is a special case, being a congener of cyclopentadiene which forms compounds of unusual stability with the transition elements. The effect of changes in the X group on the stability of the phenyltitanium bond was as follows: butoxy $\simeq$ isobutoxy $\simeq$ propoxy $\simeq$ isopropoxy $>$ methoxy, chloride $>$ fluoride. Study of changes in n showed that greatest stability was obtained when $n = 1$. Stability fell off sharply when $n = 2$, and quadrivalent compounds were virtually nonexistent with more than two R groups bound to the titanium atom. However, lower valent compounds of titanium which still contained carbon-metal bonds were indicated.

To establish more firmly the identity of the organic derivatives of reduced titanium and to examine their catalytic activity, phenylmagnesium bromide was added to butyl titanate and titanium tetrachloride at 1 to 1 to 4 to 1 molar ratios. Decomposition rates are shown in Figure 1, and a summary of the data obtained at the 4 to 1 molar ratios is given in Table I. In the reactions of phenylmagnesium bromide and butyl

Table I. Reaction of 4 Moles of Phenylmagnesium Bromide with 1 Mole of Butyl Titanate and 1 Mole of Titanium Tetrachloride

(% distribution of phenyl groups after storage)

	Reaction I, Butyl Titanate						
	2-Hr. Storage			20-Hr. Storage			
	Free in ether soln.	Bound in solid with Ti, Mg, Br, Bu	Total	Free in ether soln.	Bound in solid with Ti, Mg, Br, Bu	Total	Reaction II, Titanium Tetrachloride, 20-Hr. Storage, Total Recovery
Phenyl recovered as							
Unreacted Grignard	10.5	—	10.5	2.0	—	2.0	2.4
Benzene	17.6	16.0	33.6	23.2	11.2	34.4	23.5
Biphenyl	19.5	7.0	26.5	24.3[a]	7.5	31.8[a]	50.0
Other aromatics	—	13.9	13.9	—	14.7	14.7	
Total recovery		36.9	84.5		33.4	82.7[a]	75.9

[a] 2% higher values obtained in a duplicate run.

titanate at 1 to 1 and 2 to 1 molar ratios, both monophenyl—e.g., $C_6H_5TiX_3$—and diphenyl—e.g., $(C_6H_5)_2TiX_2$—titanium species of quadrivalent titanium were formed (*8*). At higher ratios of reactants, the reactions are complicated in that decomposition of the quadrivalent organotitanium compound leads to the formation of reduced titanium compounds which may be arylated. Equations 5 to 8 are postulated.

$$n\text{RMgX} + \text{TiX}_4 \rightarrow \text{R}_n\text{TiX}_{4-n} \quad (5)$$

$$\text{R}_n\text{TiX}_{4-n} \rightarrow \text{R}_{n-1}\text{TiX}_{4-n} + \text{R}\cdot \quad (6)$$

$$\text{R}_{n-1}\text{TiX}_{4-n} + \text{RMgX} \rightarrow \text{R}_n\text{TiX}_{3-n} \quad (7)$$

$$\text{R}\cdot \rightarrow \text{organic by-products} \quad (8)$$

To establish the validity of these equations, the following factors must be determined: completeness of utilization of the Grignard reagent, extent of reduction of the organotitanium compounds, identity of the purely organic products of decomposition, and identity of the titanium products of the decomposition, particularly these reduced titanium products which are still organometallic in nature. Finally, it was necessary to relate the various identifiable products to the individual equations shown.

Diagnostic experiments were carried out. The product was carbonated to determine the extent of Grignard reagent reacted. The unbound purely organic material was separated by filtration from the solid organometallic products before any hydrolysis or oxidation was allowed to take place. The organotitanium product was hydrolyzed subsequent to the removal of the unbound organic material. The organic material so liberated was isolated and related to the initial presence of organotitanium compounds. Oxidation followed by hydrolysis was also used similarly (Equations 2 and 3).

The values listed in Table I are the per cents of the phenyl groups originally charged as Grignard reagent which are isolated in the forms indicated. A total recovery of 100% would indicate a complete accounting for all the Grignard reagent. Actually recoveries range from 82 to 84%, which is entirely satisfactory in view of the number of steps involved and the difficulty of handling these materials. In a reaction mixture (Reaction I) which was analyzed 2 hours after completion of the addition of the Grignard reagent, carbonation showed that 88 to 90% of the Grignard had been utilized. Further storage for a total of 20 hours showed that this utilization increased to 98%. The reaction is therefore very rapid and essentially complete. Any organo-

metallic material found at this point must be organotitanium in nature. Analysis of the valence levels of the titanium products shows that complete reduction to the titanous state has taken place within the 2-hour period. The term titanous includes both bi- and trivalent titanium. In the 20-hour reaction, such a reduced product contained 88% trivalent and 12% bivalent titanium compounds. Assuming that each equivalent of Grignard reagent is capable of reducing the valence level of titanium by one unit, 1.12 equivalents of Grignard reagent should be involved in reduction out of the 4 moles consumed. Therefore, slightly more than one equivalent of phenyl should be isolated as aromatic hydrocarbons, and between two and three equivalents should be bound to titanium in the titanous state as an organometallic compound. However, in Reaction I a total of 37.1% of the phenyl equivalents (17.6% benzene, 19.5% biphenyl) were isolated from the filtered ether solutions. This value increases to 47.5% on storage for 20 hours. Equating this latter quantity to a reduction reaction means that almost 2 moles of reagent have been consumed. Therefore, the titanium should be reduced completely to the bivalent state. As this was not the case, it appears that part of the Grignard reagent is destroyed catalytically by the titanium compounds. This effect is even more striking when titanium tetrachloride (Reaction II) is used in place of butyl titanate.

The solid portion of the product contained over 90% of the titanium and magnesium used in the reaction. Because this had been separated already from the ether solution and washed, all free benzene and biphenyl formed during reduction should have been removed. Any additional organic material formed on hydrolysis must be attributed to the presence of organotitanium compounds in the titanous state. Analysis of Reaction I after 2 hours shows that 36.9 mole % of the phenyl equivalents used were bound to the titanium. This material was isolated as 16.0% benzene, 7.0% biphenyl, and 13.9% high boiling aromatic residue. Analysis of the 20-hour run showed that 33.4 mole % of the phenyl equivalents used were bound to the titanium.

In the 2-hour run an average of 1.49 phenyl groups were bound to each titanium atom. This drops to 1.3 phenyl groups per titanium on storage for 20 hours. From these figures and from the analysis of the valence levels of titanium, the following compounds are indicated: $C_6H_5TiX_2$, $(C_6H_5)_2TiX$, and $(C_6H_5)TiX$. The decrease of bound phenyl groups on storage indicates a slow breakdown of these compounds. By increasing the storage time from 2 to 20 hours, the as yet unreacted portion of the Grignard reagent is consumed and gives an approximately equivalent amount of biphenyl without any apparent change in the valence levels of the titanium. A discrepancy has been shown between the extent of reduction of the titanium and the amount of organic material obtained which can be equated to reduction. All of this indicates catalytic destruction of the Grignard reagent by the titanium compounds, which takes place after the titanium has been reduced to lower valence levels. This may be explained by picturing that in an organic system the titanium is not reduced below a valence level of between two and three; once this level is reached, the titanium is reoxidized by reaction with the solvent. Continued reaction of the oxidized material with Grignard reagent is then possible.

The following types of reactions are postulated:

$$RTiX_2 \rightarrow R\cdot + TiX_2 \tag{9}$$

$$TiX_2 + C_2H_5OC_2H_5 \rightarrow TiX_2OC_2H_5 + C_2H_5\cdot \tag{10}$$

$$TiX_2 + HR \rightarrow TiX_2H + R\cdot \tag{11}$$

$$TiX_2OC_2H_5 + C_6H_5MgBr \rightarrow C_6H_5TiX_2 + C_2H_5OMgBr \tag{12}$$

$$TiX_2H + C_6H_5MgBr \rightarrow \begin{cases} C_6H_5TiX_2 + MgHBr \\ C_6H_5TiHX + MgXBr \end{cases} \tag{13}$$

Equations 10 and 11 are hypothetical reactions showing oxidation of the bivalent titanium compounds by either diethyl ether or a hydrocarbon solvent. Equations 12

and 13 illustrate the continued reaction with the Grignard reagent. The products formed go back into the cycle which starts with Equation 9. Such a scheme is similar to that used by Kharasch (*9*) to explain the apparent catalytic decomposition of phenylmagnesium bromide by cobalt chloride in the presence of bromobenzene. In this case, a cobalt subhalide, CoX, is assumed to be a carrier for a chain reaction. CoX is constantly regenerated to CoX_2 by extracting the bromine of bromobenzene. Extraction of a hydrogen by bivalent titanium is well known in the case of oxidation by water. Further support for the extraction of hydrogen by reduced metal compounds is the formation of nickel hydride in the reaction of phenylmagnesium bromide, nickel chloride, and hydrogen (*15*).

Infrared techniques can be used as a diagnostic test for the presence of the phenyl group linked to titanium. A series of bands at 3.2, 9.3, 10.7, 12.1, 13.8, and 14.3 microns is found in phenyltitanium triisopropoxide, which disappear on oxidation. The oxidation product is shown to be phenoxytitanium triisopropoxide by comparison with the spectra of a known sample. The various bands are believed to be characteristic of strains imposed on the phenyl ring in being bound to titanium rather than of the titanium-carbon bond itself. Comparison with the absorption spectra of "sandwich" cyclopentadienyl titanium compounds suggests a type of delocalized bonding. This work will be described in detail in another publication.

Most quantitative data concerning the compounds of class R_nTiX_m have been obtained in the reaction of phenyl Grignard with butyl titanate or titanium tetrachloride. This reagent was selected because of its ease in handling and the ease with which products could be identified. In working with other Grignard reagents and organoaluminum and lithium compounds, similar reactions are indicated qualitatively. A notable difference was the unusual stability in reactions with organolithium compounds. This probably results from complexing action, which was first noted by Herman and Nelson (*8*) and later reported by Friedlander and Oita (*6*) in reactions with alkyllithium compounds.

Organometallic reagents which are considered alkylating or arylating agents should form compounds of the class R_nTiX_m when reacted with titanium esters or halides. The reactions occur at room temperature and are very rapid. With the exception of stabilization by complexing action, stability of the R-Ti compounds in the quadrivalent state falls off rapidly with increases in n. However, stability is considerably greater for the bi- and trivalent compounds. In reactions of organometallic reagents at up to a 4 to 1 molar ratio, compounds of the $RTiX_2$, R_2TiX, and RTiX types are indicated. The lower valent titanium compounds appear to be free radical in nature and by virtue of an odd electron are capable of reacting with the solvent. Complete reduction to the bivalent state is not realized under the conditions examined. Titanium is reduced by a scission of the carbon-metal bond to yield free R radicals and generally insoluble highly reactive titanium compounds of lower valence.

Compounds of the class R_nTiX_m act as catalysts for the polymerization of styrene butadiene, ethylene propylene, and others. Since Ziegler's announcement (*18*) in 1954 of the low pressure polymerization of ethylene, many laboratories have been studying catalysts consisting of mixtures of various organometallic reagents with titanium halides or esters. Organotitanium compounds of the type described are postulated as playing a dominant role in this type of polymerization.

The characteristic reactions of R-Ti bonds, such as homolytic scission and the chain reaction shifts in valence level, may be responsible for the initiation of polymerization.

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Chemistry and Uses of Titanium Organic Compounds

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Tetraortho esters of titanium are produced by the reaction of titanium tetrachloride, alcohol, and ammonia. The physical and chemical properties of the *n*-alkyl and branched-chain titanates are discussed among others in the light of the coordination behavior of titanium. The esters are chemically reactive, undergoing hydrolysis, alcoholysis, acidolysis, and ester exchange reactions readily. Titanium chelates and acylates can be prepared from titanium esters. The chelates are much less reactive than the esters, but usually undergo the same reactions at higher temperatures. The acylates are polymers of low molecular weight. The uses of alkyl titanates in the paint, bonding, catalysis, and water repellency fields are stressed with emphasis on the distinct property which renders them acceptable.

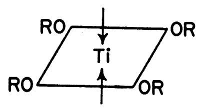
The first titanium organic compound produced was the ethyl ester prepared in 1875 by Demarcay (*14*) from titanium tetrachloride and sodium ethylate. There is some question as to whether tetraethyl titanate was obtained, but there seems little doubt that a condensed ester, at least, was prepared. In 1892 Levy (*39*) published an extensive paper describing the synthesis and properties of tetraphenyl titanate and other aryl titanates and also described attempts to produce titanium alkyls by reaction of titanium tetrachloride or titanium metal with zinc, aluminum, and mercury alkyls.

In 1924 Bischoff and Adkins (*3*) described the synthesis of tetraisopropyl titanate and tetra-*n*-butyl titanate. Little industrial attention was given titanium organics until 1947, when Kraitzer, McTaggart, and Winter (*35*) described a high temperature paint produced from tetrabutyl titanate and aluminum flake.

At about this time titanium tetrachloride began to be produced in large quantities incidental to titanium metal and titanium dioxide pigment manufacture. This large volume supply of titanium tetrachloride provided the impetus for industrial research on titanium organics and for the last 10 years an increasing amount of research has been devoted to titanium organics of a variety of types. These efforts have not led as yet to any large scale uses, but have developed a number of small industrial applications in a wide variety of fields.

Titanium Esters

The physical and chemical properties of titanium esters are influenced to a large extent by the fact that titanium has a maximum coordination number of 6, two more than its maximum valence. The structure of a tetraortho ester:



illustrates the octahedral structure the ester is capable of assuming, if it has a coordination number of 6. The two potential secondary bonds form if an electron-donating atom such as oxygen or nitrogen is available.

Thus, esters which have unshielded oxygen atoms are largely associated (*9, 10, 12*) and show unexpectedly high boiling points, densities, viscosities, and refractive indices. The formation of intermediate complexes with various materials such as water, alcohol, organic esters, and acids undoubtedly is the mechanism by which titanium esters readily undergo reaction with these compounds. The compatibility of titanium esters with such a wide variety of polar solvents is due to association with these solvents and the surface activity exhibited by titanium esters is caused by their attraction to polar surfaces.

The fact that the maximum coordination number of titanium is higher than its valence does not make it unique among metals. This situation exists with most metals; but a combination of a maximum coordination number of 6 and of steric effects due to the relatively small size of the titanium atom with four groups surrounding it (due to its valence) does provide a certain uniqueness.

Zirconium esters with a valence of 4 and maximum coordination number of 8 and aluminum esters with a valence of 3 and maximum coordination number of 6 form secondary bonds much more extensively and tenaciously than do titanium esters, thus having noticeably different physical and chemical properties. Silicon does not usually coordinate higher than its valence (except with fluorine) and silicon esters are therefore much less reactive chemically than titanium esters and have very different physical properties. The properties of titanium esters lie between those of aluminum and zirconium esters on one hand and silicon on the other.

Production of Titanium Esters. Titanium esters are prepared from titanium tetrachloride, alcohol, and a base. The reaction of titanium tetrachloride with alcohol alone will not proceed beyond the replacement of two chlorine atoms.

$$TiCl_4 + 2ROH \rightarrow TiCl_2(OR)_2 + 2HCl \qquad (1)$$

The addition of acid acceptors such as sodium alcoholate, ammonia, or amines results in the formation of the tetraester. Industrially, the Nelles process (*40*) utilizing ammonia is used.

$$TiCl_4 + 4ROH + 4NH_3 \rightarrow Ti(OR)_4 + 4NH_4Cl \qquad (2$$

The reaction is exothermic and external cooling is necessary. Usually the reaction is carried out in a hydrocarbon solvent from which the insoluble ammonium chloride is removed by filtration. The solvent is distilled off and the residual titanium ester is vacuum distilled.

Variations of this process have been patented in which the reaction is carried out in liquid ammonia (*28*) or solvents such as formamide (*29*). In these cases the ammonium chloride is soluble in the solvent, but the titanium ester separates as a distinct layer.

Alcohols such as *tert*-butanol or allyl alcohol which react readily with hydrochloric acid to produce the alkyl chloride and water do not give titanium esters by this process, because the water formed hydrolyzes the product. Titanium esters of such alcohols are

best produced by first saturating the titanium tetrachloride with ammonia to obtain the complex and reacting this with the alcohol (*22*).

$$TiCl_4 + 8NH_3 \rightarrow TiCl_4 \cdot 8NH_3 \quad (3)$$

$$TiCl_4 \cdot 8NH_3 + 4ROH \rightarrow Ti(OR)_4 + 4NH_4Cl + 4NH_3 \quad (4)$$

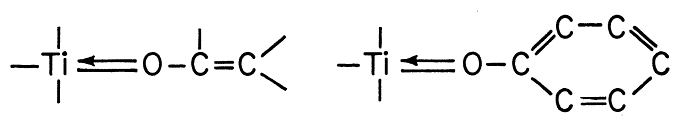
Physical Properties. The physical properties of a few titanium esters are shown in Table I.

Table I. Physical Properties of Titanium Esters

$Ti(OR)_4$ Where R Is:	M.P., °C.	B.P. °C.	B.P. Mm.	d_{25}	Visc. at 25° Cps.	Soly. in Benzene
Me	210	243	52	—	—	Insol.
Et	>25	145	8.5	1.1066	—	∞
i-Pr	20	58	1	0.9550	2.29	—
tert-Bu	—	62–3	1	0.8841	3.48	—
sec-Bu	—	90–2	1	0.9258	1.99	—
i-Bu	—	141	1	—	—	Sol.
n-Bu	<−40	134–6	1	0.9951	72.03	∞
2-Et hex	<−25	194	0.25	0.9310	147.9	—
Stearyl	64	—	—	—	—	Sol.

Methvl titanate is a high melting solid, insoluble in most solvents, properties which are due to the high degree of association of this ester. Ethyl titanate is usually seen as a liquid supercooled below its true melting point (*11*). The effect of the tertiary and secondary alkyl groups in shielding the oxygen and thereby preventing association is very noticeable in the butyl esters. The boiling points, densities, and viscosities of *tert*-butyl and *sec*-butyl titanates are very much lower than those of *n*-butyl titanate in which the *n*-butyl group does not shield the oxygen and therefore permits association.

Aryl titanates and titanates with a vinyl structure (*24*) are orange or red. All titanium compounds absorb in the near ultraviolet and absorption spectra of aryl titanates show that this has been shifted into the visible region in these compounds. This shift may be due to "back coordination" to produce the following structures:



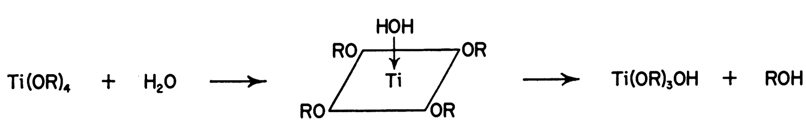
If this Ti ⇇ O bond exists, it probably does so because of the stabilizing effects of resonance with the benzene ring or the vinyl double bond. Benzyl titanate and allyl titanate in which resonance of this type would not take place are colorless.

Mixed titanium esters can be prepared, but cannot usually be isolated because ester exchange takes place very readily.

$$2Ti(OR)_2(OR')_2 \rightleftharpoons Ti(OR)_4 + Ti(OR')_4 \quad (5)$$

Undoubtedly a mixed ester is a mixture of all possible combinations—i.e., $Ti(OR)_n(OR')_{4-n}$ where n is 0 to 4.

Hydrolysis. Titanium esters hydrolyze rapidly with water from any source. The mechanism probably involves the formation of an intermediate complex (*6*) as shown in Reaction 6.



(6)

The hydroxy ester immediately reacts with an adjoining molecule to produce a condensed ester. With *n*-butyl titanate approximately 1½ moles of water can react, replacing three of the four *n*-butoxy groups before an insoluble product is obtained.

Condensed esters of varying degrees from hexaalkoxy dititanates, $[(RO)_3Ti]_2O$, to dialkoxy polytitanates, $[—Ti(OR)_2O—]_x$, can be obtained by the cautious addition of the required amount of water. An easier method of preparing the same compounds involves the use of acetic acid in place of water (Reaction 12).

Condensed titanium esters have been found (*8*) to disproportionate at elevated temperatures to give tetraortho esters and more highly condensed structures.

If very thin films of tetraisopropyl titanate (or other lower titanates) are applied to a surface and allowed to be hydrolyzed by atmospheric moisture, a clear, adherent film can be made (*27*). This film, if only air dried, contains a small amount of residual isopropoxy groups. It adheres well to polar surfaces such as cellulose, glass, metals, etc., and at the same time is itself organophilic. It has been found useful in promoting adhesion between dissimilar materials and is now in use in the production of cellophane-polyethylene, Mylar-polyethylene, and aluminum-polyethylene laminates.

Optimum adhesion is usually obtained by the addition of a small amount of another material, identical with or similar to the nonpolar component of the laminate. Thus, with polyethylene laminates a small amount of polyethylene or tetrastearyl titanate added to the isopropyl titanate gives better adhesion than isopropyl titanate alone. Commercially a 2 to 5% solution of isopropyl titanate and stearyl titanate (4 to 1 by weight) in a volatile solvent such as hexane is applied continuously to the cellophane (or Mylar or aluminum). The solvent is evaporated and the ester rapidly hydrolyzed in a high humidity oven. The polyethylene is then applied by extrusion.

A similar process has been patented for bonding silicones to various materials (*33*).

High temperature paints, using butyl titanate as the vehicle, also depend on hydrolysis of the titanate by atmospheric moisture to produce an inorganic paint. The small amount of residual butoxy groups burns off without harm to the film. When pigmented with aluminum, an inorganic paint is produced which will withstand temperatures up to 1200°F. Zinc pigmented undercoatings with an aluminum pigmented top coat give good corrosion protection for steel at temperatures up to the melting point of zinc. Condensed butyl titanate (dibutyl polytitanate) gives better films and is easier to apply than tetrabutyl titanate (*43*, *47*).

These paints give adequate protection to steel and withstand continued or intermittent high temperatures and temperature shock extremely well. They are brittle, however, and could be used only in applications where this property is not harmful. No large commercial use has developed, but the paints seem to be superior to other coatings in some applications and may eventually gain wider acceptance.

Alcoholysis. Alcoholysis of titanium esters proceeds rapidly at room temperature by a mechanism analogous to that of hydrolysis (Reaction 6). It is easy to produce higher esters from tetraisopropyl titanate by adding the stoichiometric quantity of higher alcohol and distilling off an equivalent amount of isopropyl alcohol.

$$Ti(OisoPr)_4 + 4ROH \rightleftharpoons Ti(OR)_4 + 4isoPrOH \qquad (7)$$

With hydroxyl-containing polymers such as nitrocellulose, epoxy resins, and alkyds, titanium esters react very rapidly to produce cross-linked insoluble polymers. This has been patented (*21*) and is a means of obtaining very fast, dry paints or inks. In this case the paint or ink is applied and followed immediately with a coating of titanium ester. Drying times of a fraction of a second can be obtained.

A one-coat system also is being advocated (*15*). With cellulose acetate butyrate and tetraisopropyl titanate, prior gelation can be avoided by the use of an alcohol as a solvent. The alcohol, by mass action, prevents cross linking until the lacquer is applied and the alcohol evaporated. Coatings of improved solvent resistance and heat resistance are obtained.

Acidolysis. Titanium esters react readily with organic acids according to Reactions 8 and 9.

$$Ti(OR)_4 + R'CO_2H \rightarrow Ti(OR)_3O_2CR' + ROH \qquad (8)$$

$$Ti(OR)_4 + 2R'CO_2H \rightarrow Ti(OR)_2(O_2CR')_2 + 2ROH \qquad (9)$$

The replacement of more than two alkoxy groups becomes increasingly difficult. The trialkoxy titanium acylates and the dialkoxy titanium diacylates are not stable, decomposing slowly at room temperature and rapidly at 75°C. to produce an organic ester and a condensed ester or a poly(alkoxytitanyl acylate).

$$Ti(OR)_3O_2CR' \rightarrow \left[\begin{array}{c} OR \\ | \\ -TiO- \\ | \\ OR \end{array} \right]_x + R'CO_2R \qquad (10)$$

$$Ti(OR)_2(O_2CR')_2 \rightarrow \left[\begin{array}{c} O_2CR' \\ | \\ -TiO- \\ | \\ OR \end{array} \right]_x + R'CO_2R \qquad (11)$$

These reactions using acetic acid provide a convenient method for producing condensed esters.

$$Ti(OR)_4 + HOAc \rightarrow \left[\begin{array}{c} OR \\ | \\ -TiO- \\ | \\ OR \end{array} \right]_x + ROAc + ROH \qquad (12)$$

Reaction with Acid Chlorides. Acid chlorides react with titanium esters to produce chlorotitanium esters (*32*).

$$Ti(OR)_4 + 2R'COCl \rightarrow Ti(OR)_2Cl_2 + 2R'CO_2R \qquad (13)$$

Chlorotitanium esters are best produced, however, by the reaction of stoichiometric quantities of titanium tetrachloride with titanium esters (*7, 41*).

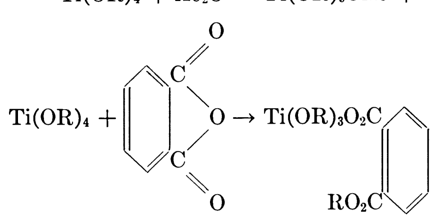
$$Ti(OR)_4 + TiCl_4 \rightarrow 2TiCl_2(OR)_2 \qquad (14)$$

Chlorotitanium esters decompose slowly at elevated temperatures to produce alkyl chlorides and condensed structures.

$$TiCl_2(OR)_2 \underset{\Delta}{\rightarrow} \left[\begin{array}{c} OR \\ | \\ -TiO- \\ | \\ Cl \end{array} \right]_x + RCl \qquad (15)$$

Reaction with Acid Anhydrides. Titanium esters react rapidly with acid anhydrides according to Reactions 16 and 17.

$$Ti(OR)_4 + Ac_2O \rightarrow Ti(OR)_3OAc + ROAc \qquad (16)$$



(17)

Further reaction may take place analogously to Reactions 10 and 11.

Reaction with Organic Esters. With organic esters, titanium esters undergo ester exchange reactions rapidly at elevated temperatures.

$$Ti(OR)_4 + 4R'CO_2R'' \rightleftharpoons Ti(OR'')_4 + 4R'CO_2R \qquad (18)$$

Reaction with Silicones and Silicols. Silicols react like alcohols with titanium

esters. Thus, isopropyl titanate and four moles of triphenyl silanol give tetrakis-(triphenylsilyl)titanate. With silanediols, copolymers can be produced (*20*).

$$Ti(OR)_4 + Ph_2Si(OH)_2 \rightarrow \left[\begin{array}{c} OR\ Ph \\ |\quad| \\ -TiOSiO- \\ |\quad| \\ OR\ Ph \end{array} \right]_x + 2ROH \qquad (19)$$

Titanium esters in catalytic amounts are effective curing agents for some silicone resins (*34*). Low temperature curing for silicone textile water repellents can be accomplished by titanium ester catalysts (*19*).

Titanium esters are used with silicones as water repellents for leather (*13*). In this case no chemical reaction seems to be involved and the action of the titanium ester may be one of surface activity to provide better wetting of the leather fibers.

Catalysis by Titanium Esters. Titanium esters are excellent ester exchange catalysts for reactions both between an organic ester and an alcohol and between two organic esters.

$$R'CO_2R + R''OH \xrightleftharpoons{Ti(OR)_4} R'CO_2R'' + ROH \qquad (20)$$

$$R'CO_2R + R''CO_2R''' \xrightleftharpoons{Ti(OR)_4} R'CO_2R''' + R''CO_2R \qquad (21)$$

Table II gives the comparative rates of ethanol production in the reaction of ethyl benzoate with butanol and various catalysts.

Table II. Reaction of Ethyl Benzoate with Butanol

Catalyst Used	Concn., %	Rate of EtOH Removal, Cc./Hr.
Tetraisopropyl titanate	5	>280
Aluminum triisopropoxide	5	70
Sodium ethylate	5	50
Tetraethyl silicate	5	10
Tetrabutyl zirconate	5	0
Tributyl borate	5	0

Titanium esters are enjoying increasing commercial use as catalysts in ester exchange reactions.

Aldol condensations are effected by titanium esters (*26*). A solution of tetraisopropyl titanate in acetone, allowed to stand for several days at room temperature, will show deposits of crystals of the titanate of diacetone alcohol. At higher temperatures, the reaction goes more rapidly to produce diacetone alcohol, triacetone dialcohol, and/or mesityl oxide.

Titanium esters catalyze Meerwein-Ponndorf reactions, but do not seem to be as effective as aluminum esters. However, benzaldehyde and isopropyl titanate give near quantitative yields of dibenzalacetone. The formation of this compound must involve first a Meerwein-Ponndorf reaction to produce acetone, followed by an aldol condensation of this with benzaldehyde and dehydration to dibenzalacetone.

Pyrolysis of Titanium Esters. Titanium esters pyrolyze at temperatures of around 350°C. and higher. The primary decomposition products with isopropyl titanate seem to be propylene, isopropyl alcohol, and titanium dioxide.

If the pyrolysis is carried out by impinging an air stream (or nitrogen) containing a low concentration of tetraisopropyl titanate vapor on a hot surface (500° to 600°C.), a clear titanium dioxide film can be deposited. Such films are considerably harder than those produced by hydrolysis of titanium esters and contain no residual organic matter.

Titanium dioxide films produced by pyrolysis of titanium esters show promise as scratch-resistant coatings on glass containers.

Titanium Chelates

Titanium chelates formed in aqueous systems such as titanium oxalate, titanium glycolate (*36*), and glyceryl titanate (*4*) have been known for a number of years. They have not found commercial use.

More recently attention has turned to chelates formed in nonaqueous systems. The heat of formation of dichelates from tetraisopropyl titanate seems to be between 15 and 20 kcal. Their formation takes place readily therefore, and their synthesis usually involves merely mixing 2 moles of ligand with 1 mole of titanium tetraester.

In these cases the ligands contain hydroxyl groups which by alcoholysis replace two alkoxy groups of the titanium ester. An electron-donating group is on the second or third carbon from that to which the alcohol group is attached, so that a five- or six-membered ring may be formed with the titanium atom. Strong chelates are formed by glycols such as 2-ethylhexane-1,3-diol (*5*), by diketones (*17*) such as acetylacetone, by hydroxy acids such as lactic, citric, and tartaric, by ketoesters such as acetoacetic ester, and by amino alcohols such as diethanolamine and triethanolamine.

With glycols, alcoholysis of both hydroxy groups to produce polymers is a competitive reaction to chelate formation. With most glycols polymer formation is sufficient to produce insolubility. With 2-ethylhexane-1,3-diol (octylene glycol) linking together of titanium atoms does take place (*42*) but not to a sufficient extent to produce insolubility.

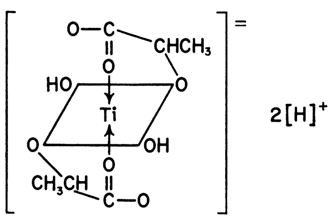
Titanium acetylacetonate, prepared from isopropyl titanate, is an orange-red compound of good stability which hydrolyzes according to Reaction 22.

$$TiAcac_2(OR)_2 + 2H_2O \rightarrow TiAcac_2(OH)_2 + 2ROH \qquad (22)$$

On air drying, the dihydroxy compound dehydrates and becomes insoluble.

$$TiAcac_2(OH)_2 \rightarrow [\text{—}TiAcac_2O\text{—}]_x + H_2O \qquad (23)$$

Titanium lactate is a white solid, easily soluble in water, which forms strongly acidic solutions stable even at prolonged boiling. The name titanium lactate is a misnomer, because the compound is not a salt of lactic acid.



The ionic structure accounts for its acidity in solution. The dried compound may be somewhat polymerized due to dehydration.

Triethanolamine titanate like octylene glycol titanate is not a definite compound; because of the multiplicity of hydroxyl groups, a certain amount of linking together of titanium atoms exists. Triethanolamine titanate is soluble in the more polar solvents such as alcohol and water. Its water solutions are strongly alkaline and hydrolyze slowly at room temperature. These solutions can be stabilized by reducing the pH to approximately 8 with carbon dioxide, phosphoric acid, or various organic acids.

In general, titanium chelates are much less reactive than titanium esters, but usually undergo the same reactions at higher temperatures. Most polymers containing hydroxyl groups are cross-linked immediately by titanium esters so that with these polymers two-coat applications must be used. With titanium chelates, however, mixed solutions of resin and chelate can be prepared which have indefinite life, but which on baking (or in some cases air drying) react to produce cross linking.

Hirt and Bruxelles (*31*) have described a system with nitrocellulose and titanium

acetylacetonate which produces on air drying a cross-linked film of improved properties. Octylene glycol titanate will react similarly and has the advantage of lighter color than the titanium acetylacetonate.

Alkanolamine titanates have been patented as cross-linking agents for epoxy resins (*2*). Various ligands added to resin-titanium ester compositions have been found to prevent prior gelation of the solution. Ethyl lactate and ethylene glycol monoethyl ether have been described as effective with cellulosics (*1*).

Titanium lactate and poly(vinyl alcohol) form stable mixed aqueous solutions. After application a short bake at 80° to 100°C. produces a film which although softened by water is no longer soluble in water.

Similar applications have been described with phenolic resins, epoxy resins, alkyds, and cellulosics (*16, 44*).

Octylene glycol titanate is an effective surface active agent in organic systems and is used with paraffin wax in textile water repellants (*18*). It gives more complete wetting of the fibers in the wax solution and therefore improved water repellency.

Titanium Acylates

Preparation and Structure. Titanium tetraacylates can be prepared, but undergo slow decomposition at room temperature to give the acid anhydride and poly(titanyl diacylates).

$$TiCl_4 + 4NaO_2CR \rightarrow Ti(O_2CR)_4 + 4NaCl \tag{24}$$

$$Ti(O_2CR)_4 \rightarrow \left[\begin{array}{c} O_2CR \\ | \\ -TiO- \\ | \\ O_2CR \end{array} \right]_x + (RCO)_2O \tag{25}$$

Poly(hydroxytitanyl acylates) can be prepared from aqueous titanyl chloride solutions (*37*).

$$TiOCl_2 + RCO_2H + H_2O \rightarrow \left[\begin{array}{c} O_2CR \\ | \\ -TiO- \\ | \\ OH \end{array} \right]_x + 2HCl \tag{26}$$

Poly(alkoxytitanyl acylates) can be prepared from titanium esters (*23, 38*).

$$Ti(OR)_4 + 2R'CO_2H \xrightarrow[\Delta]{} \left[\begin{array}{c} O_2CR' \\ | \\ -TiO- \\ | \\ OR \end{array} \right]_x + R'CO_2R + 2ROH \tag{27}$$

or

$$Ti(OR)_4 + R'CO_2H + H_2O \rightarrow \left[\begin{array}{c} O_2CR' \\ | \\ -TiO- \\ | \\ OR \end{array} \right]_x + 3ROH \tag{28}$$

All of these poly(titanyl acylates), of low molecular weight, are probably mostly cyclic structures. Although cryoscopic determinations often show no measurable depression in the freezing point of the solvent, this is due to association (as in the case of esters) rather than to a high degree of polymerization. Liquid compounds of this type such as poly(isopropoxy titanyl oleate) are not very viscous. All of the poly(titanyl acylates) are very soluble in hydrocarbons and other nonpolar solvents to give nonviscous solutions even at 50% or at higher concentrations; therefore the degree of polymerization must be low.

Reactions. Poly(alkoxytitanyl acylates) are readily hydrolyzed to poly(hydroxytitanyl acylates) by contact with water at room temperature.

$$\left[\begin{array}{c} O_2CR' \\ | \\ \text{—TiO—} \\ | \\ OR \end{array}\right]_x + H_2O \rightarrow \left[\begin{array}{c} O_2CR' \\ | \\ \text{—TiO—} \\ | \\ OH \end{array}\right]_x + ROH \quad (29)$$

When the acylate group is butyric or larger, further hydrolysis resulting in the removal of the acylate group takes place very slowly or not at all with water alone. However, aqueous sodium hydroxide solutions rapidly and completely hydrolyze all titanium acylates.

The poly(alkoxytitanyl acylates) easily undergo alcoholysis to replace the alkoxy group.

$$\left[\begin{array}{c} O_2CR' \\ | \\ \text{—TiO—} \\ | \\ OR \end{array}\right]_x + R''OH \rightleftharpoons \left[\begin{array}{c} O_2CR' \\ | \\ \text{—TiO—} \\ | \\ OR'' \end{array}\right]_x + ROH \quad (30)$$

Poly(titanyl diacylates) also readily undergo acidolysis (*25*).

$$\left[\begin{array}{c} O_2CR \\ | \\ \text{—TiO—} \\ | \\ O_2CR \end{array}\right]_x + 2R'CO_2H \rightleftharpoons \left[\begin{array}{c} O_2CR' \\ | \\ \text{—TiO—} \\ | \\ O_2CR' \end{array}\right]_x + 2RCO_2H \quad (31)$$

Uses. Poly(titanyl acylates) are excellent surface active agents and have been examined as grinding aids in pigment manufacture and as dispersants for pigments in paints, inks, and plastics. Poly(isopropoxytitanyl stearate) has shown promise as a water repellent for masonry.

Acylates made from drying oil acids such as soybean or linseed acids air dry, but the films produced are not of good quality. They have been incorporated into conventional paint coatings to give better wetting and adhesion.

Organotitanium Compounds

Levy (*39*) described attempts to make ethyl titanium in 1892 and since then many other experiments have been made. All of these early efforts resulted in a reduction in the valence of titanium, and biphenyl was isolated in work involving metallophenyl compounds. It became apparent that quadrivalent titanium compounds containing Ti—C bonds were formed, but that they immediately decomposed to give lower valent titanium and an organic radical.

In 1952 Herman and Nelson (*30*) described the synthesis of triisopropoxy phenyl titanium, a compound stable enough to be isolated. Their efforts to produce other alkyl and aryl titanium isopropoxides led them to the conclusion that the stability of the compound increased with the electronegativity of the organo group. No alkyl titanium compounds were found stable enough to isolate.

Recently, the reaction products of titanium tetrachloride and metal alkyls have come into prominence as catalysts for the preparation of linear polyethylene (*48*). These catalysts do not differ materially from the reduced titanium compounds which have resulted from the many efforts to synthesize organotitanium compounds over the years. The "new" catalysts have not been definitely identified, but may be alkyl titanium compounds where the valence of titanium is 2 or 3.

Titanium forms stable "sandwich" compounds with cyclopentadienyl groups. Dicyclopentadienyl titanium dichloride (*46*) is a stable, red crystalline compound of ionic character. It is inert to water and can be recrystallized from it.

Dicyclopentadienyl titanium diphenyl (and other dicyclopentadienyl titanium diaryls) have been produced (*45*) from dicyclopentadienyl titanium dichloride and phenyllithium, but the stability of this compound is considerably less than that of the dichloride.

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Properties and Uses of Organic Titanates

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Alkyl titanates obtained from titanium tetrachloride can undergo the following reactions among a variety of other chemical reactions: ester exchange, hydrolysis or pyrolysis to polymers, and coordination with atoms possessing unshared electron pairs. The chelates can be tailor-made to specific purposes; the most widely known are those of the amino alcohols, polyols, and hydroxy acids.

From its position in the periodic table, titanium might be expected to exhibit a close similarity to the better known "organic" elements of group IV, such as carbon and silicon as well as germanium, tin, and lead. However, this expected similarity must be modified with the recognition that titanium, zirconium, hafnium, and thorium are also in the subgroup of group IV—that is, they are transition elements. An examination of the electronic configuration (Table I) shows that the 4-valence electrons of

Table I. Electronic Configuration of Group IV Elements

Principal quantum number	1	2		3			4	
Serial quantum number	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*
C	2	2	2					
Si	2	2	6	2	2			
Ti	2	2	6	2	6	2	2	
Ge	2	2	6	2	6	10	2	2

carbon, silicon, germanium, tin, and lead are all found in the same principal quantum level, while those of the transition elements are divided between two principal quantum levels, in the case of titanium, the $3d$ and the $4s$ levels.

The $2s$, $2p$ and the $3s$, $3p$ electronic levels of carbon and silicon, respectively, are known to yield compounds having tetrahedral structures. However, the $3d$, $4s$ electron distribution of titanium could not be expected to have such a structure. The consequences of this difference in electron configuration are readily found when one compares the chemical and physical properties of compounds of the elements of the two subgroups of group IV. Such comparisons have recently been the subject of extensive studies as reviewed by Wardlaw (*9*).

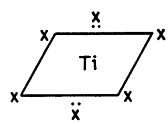
A comparison of the boiling points of the metal chlorides of elements of group IV is sufficient to show the consequences of the different electronic configurations (Table II).

A similar series of properties is found for the alkoxides of the metals. The fact that the boiling points of the chlorides and alkoxides of the titanium subgroup of group IV are considerably higher than might be expected is attributable to the much stronger intermolecular bonding forces in these compounds than in the compounds of other members of this group. The exact molecular structure of the titanium alkoxides is not known and therefore is given no further consideration here.

Table II. Boiling Points of Group IV Chlorides

Element		Boiling Point, °C.	
C		76.8	
Si		57.6	
	Ti		136.4
Ge		83.1	
	Zr		300 (subl.)
Sn		114.1	

For present purposes an octahedron, as shown, is sufficient, because in the presence of any atoms containing unshared pairs of electrons, such a structure seems reasonable for titanium compounds.



In cases where strong intermolecular attractions are found among titanium compound molecules, this structure represents coordination of the ligand atoms of one molecule with the titanium atom of a second molecule and this can be repeated through still more molecular units, leading to a sort of coordinately bonded polymer.

One principle of titanium chemistry seems to stand out—namely, the driving force of quadrivalent titanium reactions tends to increase the coordination number to 6. That is, molecules containing fourfold coordinated titanium atoms are inherently very reactive, while those containing sixfold coordinated atoms are relatively stable as exemplified by the very inert rutile structure.

The simple titanium alcoholates are examples of fourfold coordinated titanium compounds, although even here strong intermolecular attractions are found in some cases, thus permitting the titanium atoms to satisfy their coordination requirements.

Reactions of Organic Titanates

General Reactions. The alcoholates are in general very reactive, undergoing interchange with almost all molecules containing active hydrogen atoms such as alcohols, phenols, acids, and enolizable substances.

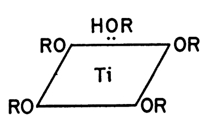
$$(RO)_4Ti + Hx \rightleftharpoons (RO)_3TiX + ROH$$

$$(RO)_4Ti + HOH \rightleftharpoons (RO)_3TiOH + ROH$$

$$(RO)_4Ti + HOR' \rightleftharpoons (RO)_3TiOR' + ROH$$

$$(RO)_4Ti + HO\overset{\overset{\displaystyle O}{\|}}{C}R' \rightleftharpoons (RO)_3TiO\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + ROH$$

The reactions, however, are reversible, the equilibrium point being determined by the concentration of the reactants and the relative reactivity of the two titanium compounds. The mechanism of the reactions can be postulated as involving a coordination-type intermediate:



The lability of the hydrogen atom and the acidic nature of the complex are demonstrated by the ability of these compounds to form salts with strong alkalies, as first pointed out by Meerwein and Bersin (*6*).

$$Ti(OR)_4 \cdot HOR + MOR' \rightarrow M^+Ti(OR)_5^- + HOR'$$

These were later utilized as ester exchange catalysts in the preparation of polyester resins as described in patents by Caldwell and Wellman (*2, 3*).

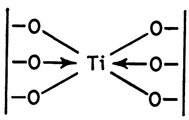
In Organic Media. One of the best studied reactions of the titanium esters, leading to a more completely coordinated state, is the reaction with macromolecules, particularly the cellulosics (*1, 4, 5, 7*). In the case of the cellulosics, such as ethylcellulose, esters, and nitrocellulose, the high concentration of oxygen atoms in these molecules permits the titanium ester molecule to attach itself very strongly to two or possibly more neighboring cellulosic chains, resulting in a cross-linking action and leading to gelation.

In this gelation, the cross linking of hydroxyl groups in the cellulosics appears to be of prime importance, but other cross links apparently also are formed, and these are probably of a coordination nature. Distinguishing between the two types of cross links is difficult, because either can lead to a gel state.

Study of solutions capable of conversion to films has been most useful in showing the importance of hydroxyl groups in the cellulosic as related to their ability to react with a simple alkyl titanate to form stable cross-linked products.

$$n\text{-Cellulosic—OH} + \text{Ti(OR)}_4 \rightleftarrows \text{(RO)Ti(O—cellulosic)}_{4-n} + n\text{-ROH}$$

In conventional solvent systems the equilibrium of this reaction is well to the right, with the resultant formation of a cross-linked gel structure, the stability of this gel probably being attributable to a coordinated state of the titanium atoms as



where the covalently bonded oxygens are supplied by hydroxyl or possibly a few carboxyl groups, while the coordinately bonded oxygens are supplied by any of the oxygens in the cellulosic, including the oxygen atoms found in the ether linkages of the cellulose chain.

Control of Cross Linking

In Presence of Alcohols. The first such method consists of using a sufficiently high concentration of an alcohol in the solvent system. This takes advantage of the reversibility of the reaction of an alkyl titanate with a cellulosic. It also permits choice of a wide variety of alcohols, each type of alcohol exhibiting a certain potential for inhibiting gel formation.

In a system containing alcohol, alkyl titanate, and cellulosic a characteristic curve is usually obtained as the ratio of alkyl titanate to cellulosic is varied. Figure 1 shows a typical curve obtained on blending butyl titanate with a medium viscosity highly ethylated ethylcellulose (Hercules Type T–50) at 10% concentration in benzene-butanol systems. The curve in general is lower as the amount of alcohol is increased. It is most significant that the lower concentrations of the titanate produce the higher viscosities. This is attributable to the relative concentrations of the alkyl titanate to the free hydroxyl groups of the cellulosic. At low titanate concentrations each titanate molecule is free to react with more than one cellulosic hydroxyl, usually on neighboring chains, thereby forming a cross link. When there is one titanate molecule for each cellulosic hydroxyl, the preferred structure is one in which only one alkoxyl group of the alkyl titanate is replaced by a cellulosic hydroxyl.

Not all alcohols exhibit comparable effectiveness in suppressing gelation. Table III lists the results obtained with a few common alcohols.

From a study of a large number of alcohols and alcohol-like materials two general rules can be expressed regarding the tenacity with which alcohols combine with titanium in a titanate ester.

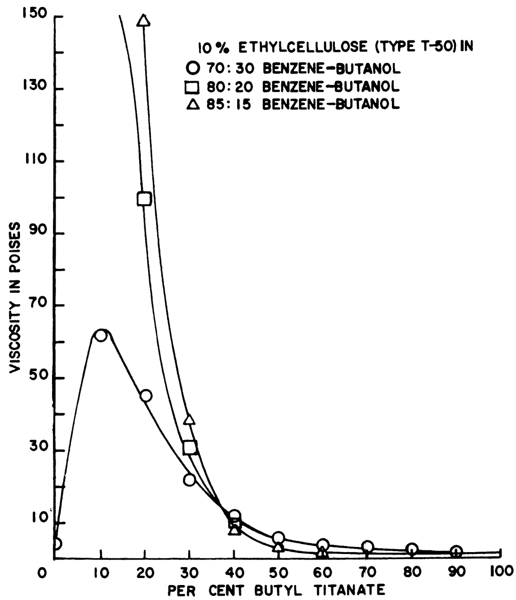


Figure 1. Effect of solvent on viscosity of butyl titanate–ethylcellulose blends

The higher the molecular weight of the alcohol, the more stable the corresponding ester.

Primary alcohols form more stable esters than secondary alcohols, which in turn combine more strongly than tertiary alcohols.

Table III. Effect of Cosolvent on Viscosity of a 50 to 50 Butyl Titanate–Ethylcellulose Blend [a]

Alcohol	Viscosity, Cps.
Methanol	Gel
Ethanol	Gel
2-Propanol	p-gel
1-Butanol	275
2-Me-propanol	300
2-Butanol	370
2-Me-2-butanol	400
Ethyl lactate	225
Ethylene glycol monoethyl ether	250

[a] Ethylcellulose (50 cps., 48.3% ethoxyl variety) at 10% concentration in 80 to 20 xylene-alcohol.

Both effects are directly attributable to shielding or the ease with which the titanate ester molecules can associate with one another or with other ligands to form a fully coordinated state of higher stability. The last two solvents in the table, the lactate ester and Cellosolve, are of particular interest, because they indicate an effect which is not connected either with size or degree of branching, but rather with the ability to form complexes probably of a weak chelate nature.

In Presence of Chelating Agents. The second general method of suppressing gel formation in a titanate-cellulosic system is by formation of true coordination compounds of a titanate ester.

A typical, yet very simple system of this type is shown in Figure 2. Here addi-

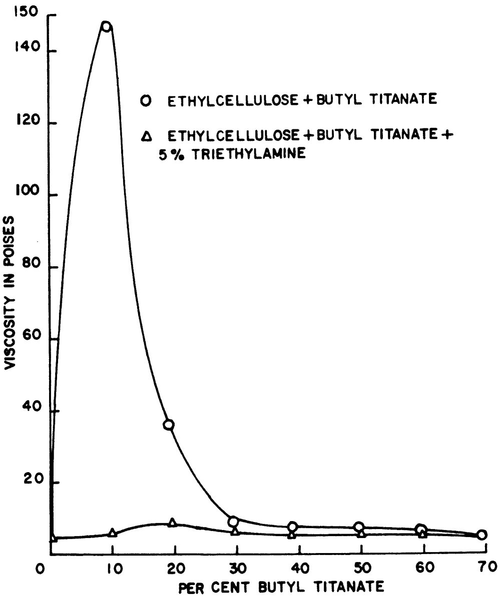


Figure 2. Effect of triethylamine on viscosity of butyl titanate–ethylcellulose blends

tion of an amine compound to the system permits formation of an amine complex with the titanium ester which thereby blocks the ester exchange reaction with the cellulosic hydroxyls (Figure 3).

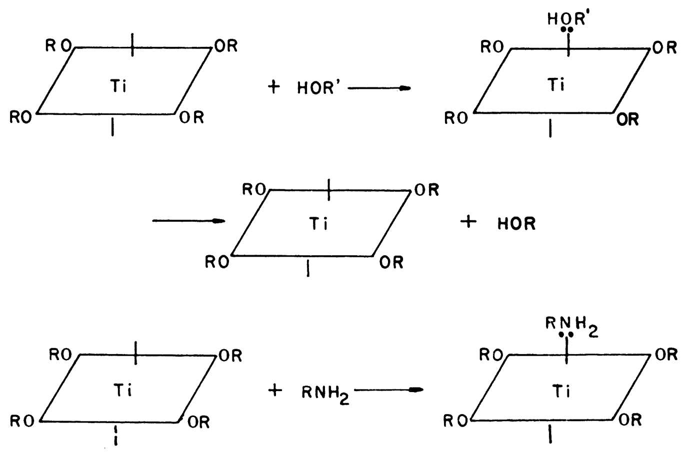


Figure 3. Ester interchange mechanism and blocking effect of amines

Amino alcohols, particularly of the diethanolamine and triethanolamine type, have an even greater effect, due to their ability to form chelates. This effect is not limited to the amine complexes; β-diketones also are effective with cellulose acetate, as shown in Figure 4. A more detailed study of the relative effects of alcohols and β-diketones as stabilizers for these systems has recently been published by Hert and Bruxelles (*5*).

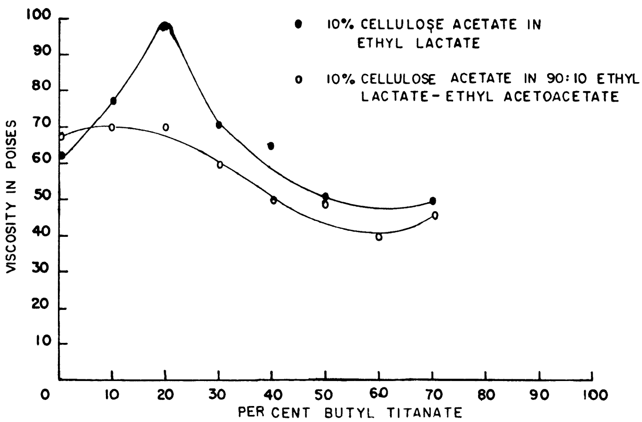


Figure 4. Effect of complexing solvents on viscosity of butyl titanate–cellulose acetate blends

Thus, two practical types of organic solvent system are available for the study of alkyl titanate-cellulosic systems: those containing alcohols and those containing chelating agents. Based on these studies attempts were made to detect similar reactions in aqueous systems.

In Aqueous Media. Alkyl titanates could not be used in the presence of water, but a number of chelates of titanium are sufficiently stable for aqueous studies, particularly those of the amino alcohols, triethanolamine, as well as those of hydroxy acids such as lactate, tartrate, citrate, and gluconate. For these studies the amino alcohol chelate was prepared by simply adding 2 moles of triethanolamine to 1 mole of isopropyl titanate. The chelates of hydroxy acids were prepared by adding 2 moles of the sodium salt of the corresponding acids to aqueous solutions of titanium tetrachloride. For comparison some unchelated salts, such as titanyl sulfate, titanium tetrachloride, and titanium dichloride-diacetate were included.

Titanium dichloride-diacetate was prepared by the vapor phase reaction of titanium tetrachloride and acetic acid as described by Wadington (*8*). This is a water-soluble titanium salt of the nonchelated type, which in aqueous solution exhibits essentially the activity of titanium tetrachloride, but does not hydrolyze at an extremely rapid rate.

With Cellulose. Using the above water-soluble titanium compounds, viscosity studies were carried out on aqueous solutions of a wide variety of water-dispersible cellulosics including various starches, methylcellulose, hydroxyethylcellulose, and carboxymethylcellulose. However, in none of these homogeneous aqueous systems was there conclusive evidence of titanium compound interaction with the cellulosic.

Previous experience with titanium dichloride-diacetate treatments of cellulose and regenerated cellulose had given evidence of a cross-linking action by the titanium compound, as indicated by the failure of the treated cellulose to dissolve in the usual solvents, such as cuprammonium and xanthate. In these treatments the acid titanium solution was applied to the fabric which was partially dried to set the treatment, neutralized, and finally dried.

A similar type of treatment was given to viscose rayon yarn using a series of water-soluble titanium compounds. The solutions at the equivalency of 100 grams per liter of titanium dioxide were applied to skeins of bright viscose yarn, the excess solution was centrifuged, and the yarn was allowed to dry until approximately half of the water had evaporated. The fibers were then neutralized in sodium carbonate solution and dried.

Evidence for a cross-linking action by the titanium compounds was found in the

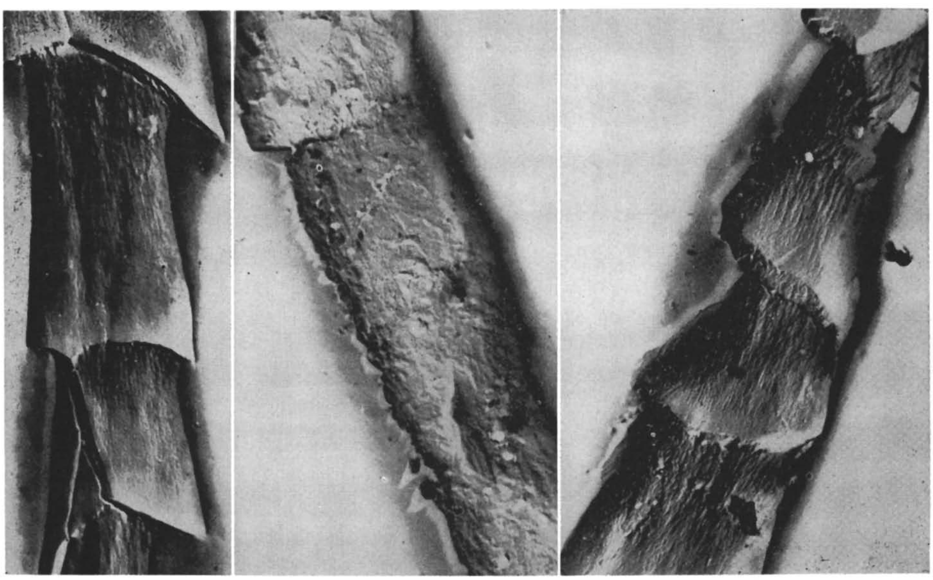
reduced water-retention values in the treated rayon yarn. The yarn samples were weighed, dried, immersed in water, centrifuged to remove excess water, and then reweighed (Table IV).

Table IV. Viscose Rayon Yarn Treatment

Titanium Compound, 100 Grams TiO_2/Liter	Water Retention, %	Ash, %
Control (no treatment)	80	0.1
Triethanolamine titanate	75	0.7
Titanyl sulfate	63	2.7
Titanium citrate	61	3.8
Titanium tartrate	57	3.9
Titanium dichloride-diacetate	51	9.8
Titanium tetrachloride	48	10.4

The degree of the reaction of titanium with cellulose in aqueous solution, as in organic solutions, is determined by the extent of coordination in the titanium compound. The most reactive compounds as indicated by both the ash content and the water retention are the uncoordinated ones, the titanium tetrachloride, and the titanium dichloride-diacetate. Titanyl sulfate shows a much lower degree of reactivity than titanium tetrachloride and it apparently resembles more closely the chelated titanium citrate and tartrate.

With Proteins. There are also indications that titanium compounds can react with proteins. As with cellulose, it has not been possible to characterize the nature of the reaction as precisely as in the case of the organic soluble cellulosics. Viscosity studies of water-soluble protein-titanium compound systems have failed to yield conclusive results. Nevertheless, proteins treated with titanium compounds in general exhibit a markedly lessened solubility and also a greater chemical resistance.



a b c

Figure 5. Micrographs of wool fibers

a. Untreated
b. Chlorinated in absence of titanate
c. Presence of titanate

Figure 5 illustrates this protective action in the case of wool treated with chlorine. Fiber *a* is from a sample of an untreated wool jersey. Fiber *b* is from a fabric sample which was treated with a 3% aqueous solution of sodium hypochlorite at pH 4 for 60 seconds, rinsed in water, and treated with 1% sodium bisulfite.

Fiber *c* is from a sample which was treated with an aqueous solution of triethanolamine titanate (10 grams of TiO_2 per liter) dried, then subjected to the same hypochlorite and bisulfite treatment as in the case of the central fiber.

The extent of the damage to the fibers can best be judged from a comparison of the two chlorinated fibers. The central fiber, *b*, has been completely denuded of scales. Fiber *c* under the same conditions shows only an attack at the edges of the scales.

The mechanism of the titanium reactions with fiber and the points of attachment remains rather obscure. It seems most probable that the titanium attaches itself first and most strongly to hydroxyl or carboxyl groups of the protein fiber. However, there are probably an insufficient number of such groups to account for the attachment of the nearly 1% titanium as titanium dioxide found in the treated fiber. It is postulated that most of the titanium is coordinately bonded to the protein, probably through amine or amide groups and by so bonding to the protein a blockage is set up which prevents oxidative and hydrolytic agents from attacking the protein chains.

Summary

Given the right conditions, titanium can attach itself to almost any high molecular weight polymer containing atoms such as oxygen and nitrogen with unshared pairs of electrons. The first point of attachment appears to be the polar groups containing active hydrogen, such as hydroxyl or carboxyl groups, but strong bonds probably can also be formed in which the attachment is primarily by coordination.

Acknowledgment

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Preparation of Tetraalkyllead Compounds from Lead or Its Alloys

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Lead is commonly alkylated by one of two basic methods: the reaction of sodium-lead alloy with an alkyl halide, or the reaction of a lead salt with an active organometallic compound. The first method is used for the commercial production of tetraethyllead, a high-tonnage chemical used as an antiknock agent. For this reason, the Ethyl Corp. has conducted research for many years on reactions based on this method. Several modifications of the basic method are outlined for the first time. Descriptions are given of the reaction of active metallic lead with alkyl halides, sulfates, and phosphates both in the presence and absence of organometallic compounds or added metals. Descriptions are also presented of the reactions of various binary and ternary alloys of lead with alkyl halides and sulfates. Factors of practical interest in these reactions are discussed.

Heavy metals such as lead are most commonly alkylated by one of two basic methods (*31*):

In Löwig's method (*32*), an alkyl halide reacts with an alloy of a heavy metal and an alkali metal, forming the halide of the alkali metal and the alkyl compound of the heavy metal.

$$4NaPb + 4RCl \rightarrow R_4Pb + 4NaCl + 3Pb \quad (1)$$

In Buckton's method (*4, 36*), the halide of a heavy metal reacts with an alkyl compound of a more electropositive metal.

$$2PbCl_2 + 2R_2Zn \rightarrow R_4Pb + 2ZnCl_2 + Pb \quad (2)$$

$$2PbCl_2 + 4RMgCl \rightarrow R_4Pb + 4MgCl_2 + Pb \quad (3)$$

Numerous other ways of synthesis have been employed, such as free radical methods, electrolytic reduction reactions, liquid ammonia preparations, and procedures involving quadrivalent lead salts. However, the second method, as modified by Pfeiffer to use the Grignard reagent, has provided both the most practical means of synthesis of organometallic compounds in the laboratory and a means of studying the chemical reactivity of the metals in question. Löwig's method, utilizing monosodium-lead alloy (*26*), is still used today for the commercial production of tetraethyllead. The sim-

plicity and high yield of this method permit production at a cost low enough to allow the economical use of tetraethyllead as an antiknock agent on a very large scale.

Löwig's method has been studied extensively, because of its commercial importance. A number of modifications of this basic method are indicated in the patent literature. This paper gives for the first time a comprehensive account of these methods. Voluminous experimental details are unnecessary for this purpose, but may be given in future publications.

Reactions of Metallic Lead

Lead with Alkyl Halides. Because the cost of sodium is an important economic factor in the production of tetraethyllead by the conventional process, a careful study was made of the direct reaction of lead metal with alkyl halides, using lead itself as the reducing or alkylating metal, as in Equation 4.

$$3Pb + 4RX \rightarrow R_4Pb + 2PbX_2 \qquad (4)$$

For active metals such as lithium, magnesium, aluminum, and zinc, this type of reaction with alkyl halides is well known.

$$M + RX \rightarrow [RMX] \rightarrow RM + MX \qquad (5)$$

However, the direct alkylation of heavy metals, like lead, is not commonly regarded as possible. Such a reaction for lead was first attempted with ethyl iodide by Cahours (*5*) in 1853, but he reported only the qualitative formation of a small amount of organolead compound, which he did not attempt to identify.

In recent work, lead metal has reacted under a variety of conditions with several alkyl halides, to form tetraalkyllead compounds in good yield. Commercially comminuted lead powders and flakes, but preferably lead formed as a residue in other organolead reactions (as in Equation 1), was found suitable for alkylation. It was shown that the metal must present a large, clean surface, free of combined or adsorbed impurities, such as air or moisture. Such active lead gave good yields with methyl bromide, methyl iodide, and ethyl iodide, but did not react significantly under uncatalyzed conditions with methyl chloride, ethyl chloride, and ethyl bromide. The preferred catalysts for these reactions were shown to be iodine and iodine-containing compounds (*35*), used in the amount of about 1 atom % of the lead. The reactivity of the alkyl halides tested decreased in the order: MeI > EtI > MeBr > MeCI > EtBr > EtCl. Good rates of reaction were obtained at 100° to 130°C. In the reaction of ethyl chloride with lead residue prepared according to Equation 1, tetraethyllead yields of about 65%, based on Equation 4, were obtained in 5 hours at 130°C., using 1.3 atom % iodine as catalyst. When commercial lead flakes reacted with ethyl chloride, the maximum yield was of the order of 30%; with ethyl iodide, the yield increased to 50%.

Not only is it possible to prepare tetramethyl- and tetraethyllead in this way, but mixed alkyllead compounds can be prepared in a random equilibrium mixture (*7*) from mixtures of methyl and ethyl chlorides. It is also possible to combine the reactions of sodium-lead alloy and lead metal into a consecutive two-step process, as in Equations 1 and 4, by raising the temperature after the reaction of the alloy, without separating the product of this reaction. The over-all process is then represented by Equation 6:

$$2NaPb + 4EtCl \rightarrow Et_4Pb + 2NaCl + PbCl_2 \qquad (6)$$

Lead with Other Alkylating Agents. Lead metal, obtained as in Equation 1, has also reacted in small-scale equipment with alkyl sulfates and alkyl phosphates (*27*), for 20 hours, to give yields of tetramethyl- or tetraethyllead of 20 to 65%, at 110° to 125°C. For the catalyst, 3 atom % lead iodide was desirable, although this was not required for the preparation of tetramethyllead. The yields were based on the equations:

$$3Pb + 2R_2SO_4 \rightarrow R_4Pb + 2PbSO_4 \quad (7)$$

$$9Pb + 4R_3PO_4 \rightarrow 3R_4Pb + 2Pb_3(PO_4)_2 \quad (8)$$

Lead with Alkyl Halides and Reducing Metal. An extended investigation was made of the alkylation of lead metal with alkyl halide in the presence of a reducing metal such as magnesium. This reaction is interesting from a commercial standpoint, in conjunction with the sodium-lead–ethyl chloride reaction. It provides a possible means of increasing the yield of tetraethyllead per charge in plant autoclaves (*10*). The reaction can be run either separately or concurrently with the reaction of Equation 1, according to the following, idealized equations:

$$Pb + 4RCl + 2Mg \rightarrow R_4Pb + 2MgCl_2 \quad (9)$$

$$4NaPb + 16RCl + 6Mg \rightarrow 4R_4Pb + 4NaCl + 6MgCl_2 \quad (10)$$

The active lead may be prepared for reaction by various means, as in Reaction 4, and the magnesium is conveniently supplied in the form of chips. About 10 to 20% of an aliphatic ether such as diethyl ether, based on the ethyl chloride present, is used as catalyst. As a result, the Grignard reagent is formed in situ from the magnesium. In 2 to 4 hours at the optimum temperature of 70°C., using an excess of ethyl chloride, tetraethyllead yields of about 75% were obtained in small-scale equipment.

Other catalysts, such as tertiary amines or alkylammonium iodides, may be employed, along with other reducing metals such as lithium (but not sodium), to give somewhat poorer yields. Other alkyl halides (methyl and propyl chlorides, bromides, and iodides) may be used as the alkylating agents for the lead metal, but preferably not in a concurrent reaction with sodium-lead alloy.

The formation of tetraalkyllead is accompanied invariably by the formation of hexaalkyldilead, which decomposes slowly to form additional tetraalkyllead and lead metal. The hexaalkyldilead remaining in the product may be converted to tetraalkyllead by subsequent thermal decomposition, or by treatment with catalysts, such as Filtrol (*34*), alkyl bromides or iodides (*28*), or activated carbon (*23A*), according to:

$$2R_6Pb_2 \rightarrow 3R_4Pb + Pb \quad (11)$$

Lead with Alkyl Halides and Organometallic Compounds. In the type of reaction described above, preformed Grignard reagent may be used in lieu of the magnesium chips (*13*). With reactions using chlorides, the reaction may be run in a single stage with a sodium-lead reaction, if desired. The equation for this preparation of tetraethylead is:

$$4NaPb + 10EtCl + 6EtMgCl \rightarrow 4Et_4Pb + 6MgCl_2 + 4NaCl \quad (12)$$

In studying this reaction, it was shown that ether is desirable, but not necessary, as a catalyst (although a catalyst of this type is vital for the reaction with magnesium metal). The reaction was carried out effectively with ethyl magnesium iodide prepared in benzene in the absence of ether. Hexaethyldilead was not formed under these noncatalyzed conditions.

Other organometallic compounds, such as ethyllithium, diethylzinc, diethylcadmium, and ethylcadmium iodide, were effective ethylating agents in reactions analogous to Equation 12. At 70°C. in small-scale equipment, yields were over 90% with the lithium reagent and ethyl chloride, but the zinc and cadmium compounds gave good yields only when ethyl iodide was employed as the alkylating agent (*14–16*). The same type of reaction was effected using "sodium-naphthalene complex" as the reducing agent (*43*). Good yields of tetraalkyllead were obtained by this method when ether- or amine-type catalyst was present, although free sodium metal and alkylsodium compounds did not yield any organolead product.

Other kinds of alkylation reactions reported in the literature may be related to the alkylation of metallic lead with alkyl halides and organometallic compounds.

Gilman (*23*) describes an elegant laboratory method for the preparation of tetraalkyllead compounds from lead chloride.

$$PbCl_2 + 3RLi + RI \rightarrow R_4Pb + 2LiCl + LiI \quad (13)$$

Retrospectively, this reaction may be classified as the direct alkylation of a metal as described above. The author has tested it experimentally, and found that in the reaction of lead chloride with methyl Grignard reagent, the Gilman reaction can be carried out either by his procedure, or in a two-step synthesis; the first step being a classical Grignard alkylation, according to Pfeiffer and Truskier (*36*):

$$2PbCl_2 + 4MeMgCl \rightarrow Me_4Pb + 4MgCl_2 + Pb \quad (14)$$

and the second, an alkylation of the separated metallic lead, in accordance with the discussion above:

$$Pb + 2MeCl + 2MeMgCl \rightarrow Me_4Pb + 2MgCl_2 \quad (15)$$

Table I summarizes representative yield data on the principal reactions of lead metal described above.

Table I. Representative Yields of R_4Pb from Metallic Lead

Lead Source[a]	Alkyl Halide	Other Reactant	Catalyst, Atom % Based on Pb	R_4Pb Yield, %
A	EtCl	—	$1I_2$	65
B	EtCl	—	$1I_2$	30
A	MeI or EtI	—	$1I_2$	70
B	EtI	—	$1I_2$	50
A	Et_2SO_4	—	$3PbI_2$	55
	Me_2SO_4	—	$3PbI_2$	65
	Et_3PO_4	—	$3PbI_2$	20
	EtCl	Mg	$10Et_2O$[b]	75
	EtCl	EtMgCl	$10Et_2O$[b]	75
	EtCl	EtLi	—	90
	EtCl	$Na(C_{10}H_8)$	$35C_6H_5N(CH_3)_2$, $80CH_3OCH_2CH_2OCH_3$[b]	20
	EtI	$Na(C_{10}H_8)$	$20C_6H_5N(CH_3)_2$, $95CH_3OCH_2CH_2OCH_3$[c]	70

[a] Lead source A is metallic lead product of reaction of NaPb with EtCl. R_4Pb yield figure is based on reaction of metallic lead in subsequent RX reaction, and does not include NaPb-EtCl product. Lead source B is commercial Metalead paste.
[b] % based on EtCl.
[c] % based on EtI.

Reactions of Lead Alloys

The commercial success of sodium-lead for the production of tetraethyllead has led to the investigation of numerous other alloys for this purpose. These compositions have comprised either binary or ternary alloys of lead. The binary alloys have consisted of other compositions with sodium or have contained other Group I or Group II metals.

Dimagnesium-Lead Alloy. One of the most interesting alloys explored is the composition dimagnesium-lead. This alloy is a well-known ionic compound of the fluorite lattice structure (*24*). Good yields of alkyllead compounds were obtained from the alloy according to:

$$Mg_2Pb + 4RX \rightarrow R_4Pb + 2MgX_2 \quad (16)$$

The reaction may be carried out with an alkyl iodide, in which case a catalyst is not required (*41*) or preferably, it may be run with an alkyl bromide or chloride (*39, 40*). When the alkylating agent was ethyl chloride, optimum yields of 85 to 90% were obtained in 2 hours at 120°C., in small bombs, using 5 equivalents of ethyl chloride and a catalyst combination of 5% ether and 85% ethyl iodide, based on alloy weight. This reaction is sharply differentiated from the reaction of lead metal with an alkyl halide and magnesium, because no hexaalkyldilead is produced as a by-product.

The alkyl chloride reaction was shown to be operable with a variety of catalysts, primary aliphatic ethers and alkyl iodides being most useful. Tetraalkyllead compounds from methyl to isopropyl and *n*-butyl were prepared by this means. The reaction of dimagnesium-lead with ether-catalyzed alkyl iodide (in the absence of alkyl chloride) appears to be a simple preparative method for use in the laboratory, once the alloy is available.

Ternary Lead Alloys. The preparation of tetraethyllead from various ternary alloys containing sodium and lead has been attempted since 1850. At that time, Löwig claimed to have prepared tetraethyllead by the reaction of ethyl iodide with sodium and lead amalgamated with excess mercury. Since then, the reaction has been attempted with sodium-lead alloys containing small amounts of lithium, potassium, magnesium, zinc, tin, copper, and silver. Appreciable additions of magnesium, potassium, and zinc have been investigated recently.

Some of the most interesting experimental work on the alkylation of lead in ternary alloys has been conducted on systems containing lead, sodium, and magnesium. This ternary metal system is exceedingly complex (*17*, *18*), and therefore has not been fully investigated. The alloys that alkylate best are located on the sodium-lead-magnesium cross section (*11*, *12*), which contains a peritectic compound of composition NaMgPb. The best of such alloys, reacted with ether catalyst and excess ethyl chloride at 85°C., gave tetraethyllead yields of about 75%, based on the combination of reducing metals present. The reaction resembled the alkylation of metallic lead in the presence of magnesium metal, because hexaethyldilead was formed as a by-product.

The replacement of magnesium in a ternary alloy by potassium is interesting (*44*). A ternary alloy containing equiatomic proportions of lead and alkali metals, in which 15 atom % of the alkali metal is potassium, is capable of giving yields of tetraethyllead of over 95%, based on both reducing metals. This compares favorably with the usual yield of about 85% from sodium-lead alloy in the conventional reaction. The potassium not only reacts, but also increases the utilization of sodium. The reaction is modified in that the formation of by-product hydrocarbons by Wurtz-type coupling reactions is almost eliminated.

Such reactions were usually run at 80° to 100°C. with excess ethyl chloride. A ketone catalyst (0.2 weight % acetone based on alloy weight) is vital to obtain good yields at normal, operating temperatures. Thus, the reaction is different in mechanism from the conventional sodium-lead–ethyl chloride reaction.

Nonasodium-Tetralead Alloy. The cost of recycling lead metal in the commercial sodium-lead–ethyl chloride process has aroused interest in the use of sodium-rich alloys for many years. Most of the sodium-lead alloys, however, are rather unreactive with ethyl chloride. The sodium-rich alloys between sodium-lead and pentasodium-dilead are progressively less reactive until at the composition of pentasodium-dilead reaction practically ceases. However, if the alkylating agent is ethyl bromide or preferably ethyl iodide, good yields may be obtained from higher sodium alloys in the presence of amines or hydroxyl compounds, such as pyridine or water (*6*). This type of so-called hydrous reaction was used commercially for a short time in the 1920's. However, the economics of such processes are unfavorable as compared with the present sodium-lead–ethyl chloride process. Therefore, the anhydrous reactions of sodium-rich alloys with ethyl chloride were reinvestigated recently.

A thermal analysis of the sodium-lead phase diagram demonstrated the existence of a hitherto unrecognized open maximum compound at the composition nonasodium-tetralead (*30*). Compositions at or below this exact level of sodium content were reactive with ethyl chloride, provided that a catalyst such as an ester, aldehyde, or ketone, was present (*2*). Yields of approximately 70% on sodium were obtained in about 2 hours at 100°C. when about 0.5% (on weight of alloy) of acetone or ethyl acetate catalyst was used. Above the sodium percentage contained in nonasodium-tetralead, the alloys became abruptly unreactive with ethyl chloride, even when catalyst was present.

Binary Lead Alloys with Calcium, Potassium, and Lithium. In addition to sodium and magnesium, binary alloys of lead with calcium (*29*), potassium, and lithium were investigated within the past several years. The compositions lithium-lead and calcium-lead were reactive with ethyl chloride, while the alloy potassium-lead gave yields of less than 20% on potassium under the best conditions tested. The alloy lithium-lead is very expensive for commercial use. Uncatalyzed, the alloy calcium-lead gave yields of 80% at 70°C., according to:

$$2CaPb + 4EtCl \rightarrow 2CaCl_2 + Et_4Pb + Pb \quad (17)$$

It is noteworthy that the composition dicalcium-lead, which is a well-defined intermetallic compound, reacted poorly.

Monosodium-Lead Alloy Reaction with Ethyl Chloride. Much of the research on the sodium-lead–ethyl chloride reaction in recent years has dealt with its acceleration or retardation. In the discussion of lead metal reactions, it was pointed out that the surface of the lead must be free of combined or adsorbed impurities. This is equally true for the alloy reactions, because here also there is a heterogeneous reaction between solid metal and liquid or gaseous alkyl halide. The reaction velocity is therefore very susceptible to surface effects.

The conventional sodium-lead–ethyl chloride reaction is sensitive to certain impurities in the ethyl chloride. As little as 0.0025% acetylene exerts a powerful retarding effect. This retardation, or poisoning as it is commonly known, has become so severe in some alloy reactions as to result in a coating on the steel walls of the reaction vessel which renders the vessel inoperable. This wall-retained poison is not always removed by scrubbing or solvent action, and sometimes it is necessary to etch the steel with acid to restore its useful condition.

In experimentation designed to increase the production of tetraethyllead, it has been discovered that the rate of the sodium-lead–ethyl chloride reaction may be increased significantly by the use of 0.005 to 4% of an accelerator, such as a ketone (*25*), aldehyde (*21*), acetal (*37*), anhydride (*22*), ester (*20*), or amide (*19*). It is also important, commercially, that such accelerators have the additional effect of offsetting the deleterious effect of minor amounts of poisons of the acetylene type.

The rate of the sodium-lead–ethyl chloride reaction is also influenced strongly by the gross structure and surface area of the alloy. Ordinary methods of comminution of the alloy to a fine state of subdivision result in a decreased rate and yield. This decrease is probably caused by contamination of the surface, inherent to the usual process of comminution. The rate can be increased markedly, however, by wet-grinding the alloy immersed in ethyl chloride at low temperature (*42*). Thus, the alloy surface can be enlarged, while it is protected until rapid reaction is desired.

The reactivity of the alloy may also be enhanced by decreasing the size of the crystals. This may be accomplished by quick-cooling, as by drum-casting (*1, 38, 47, 48*). Quick cooling may also be accomplished by feeding the alloy in the molten state to the ethyl chloride (*33*).

Monosodium-Lead Alloy Reaction with Methyl Chloride. Interest has been expressed over many years in the use of mixed methylethyllead alkyls, such as methyltriethyllead, as antiknocks, owing to their greater volatility in the engine manifold as compared with tetraethyllead. This has led to a study of methods of manufacture of tetramethyllead and the mixed methyl-ethyl lead compounds.

It has been known that none of the methyl or ethyl halides, with the exception of ethyl chloride, will react at an appreciable rate with sodium-lead alloy. Moreover, the addition of one of the other methyl or ethyl halides to this type of ethyl chloride reaction tends to poison the reaction. However, Lewis acid catalysts of the aluminum halide type, such as aluminum chloride, promote the reaction (*9*). Other catalysts, such as compounds of beryllium, zinc, boron, phosphorus, and arsenic, are also effective, but to a lesser extent. These catalysts made it possible to devise an economical process for the manufacture of tetramethyllead or mixed methylethyllead compounds

(*8*) by means of an alkylation with methyl chloride or a mixture of the corresponding alkyl halides. The reaction was usually carried out at 90° to 100°C. for 2 to 4 hours, using about 4 atom % aluminum chloride on the basis of sodium, to give yields of approximately 85%.

Sodium-Lead Alloy Reactions with Diethyl Sulfate. Efforts have been made to develop a commercial ethyl sulfate process (*46*), because diethyl sulfate is more available and less expensive as an ethylating agent than ethyl chloride. In recent experiments, the entire range of sodium-lead alloys was investigated, thus establishing the decreasing order of alloy reactivity $NaPb > Na_9Pb_4 > Na_5Pb_2 > Na_4Pb$. Using sodium-lead, yields on sodium as high as 75% were obtained in 2 hours at 120° to 130°C. in uncatalyzed reactions. With higher sodium alloys, an iodine-containing catalyst is required to obtain good yields (*45*). Pentasodium-dilead alloy gave 80% yields of tetraethyllead in 5 hours at 130° to 140°C., when 1 atom % lead iodide was present, whereas the uncatalyzed reaction gave only a 10% yield. In all such reactions, however, only one ethyl group reacted, according to:

$$4NaPb + 4Et_2SO_4 \rightarrow Et_4Pb + 4NaEtSO_4 + 3Pb \quad (18)$$

The fact that only one ethyl group is utilized in the primary reaction forces a regeneration or recovery operation. The slower rate of reaction and the higher temperatures required are also factors which make the ethyl sulfate process disadvantageous as compared with the ethyl chloride process.

Table II. Representative Yields of Tetralkyllead from Lead Alloys

Alloy Composition	Alkyl Halide	Catalyst, % Based on Alloy Wt.	R_4Pb Yield, %
NaPb	MeCl, MeBr, MeI, EtBr, or EtI	—	0
	EtCl	—	85
	MeCl	$4AlCl_3$[a]	85
Na_2Pb	EtCl	—	60
Na_9Pb_4	EtCl	—	5
Na_5Pb_2	EtCl	—	0
Na_4Pb	EtCl	—	0
Na_9Pb_4	EtCl	$0.5C_2H_5OOCCH_3$	70
Na_4Pb	EtCl	$0.5C_2H_5OOCCH_3$	0
NaPb	Et_2SO_4	—	75
Na_5Pb_2	Et_2SO_4	—	10
	Et_2SO_4	$1PbI_2$[b]	80
CaPb	EtCl	—	80
Mg_2Pb	EtCl	—	5
	EtCl	$5Et_2O$, 85EtI	85
	EtBr	—	10
	EtBr	$15Et_2O$	60
	EtI	—	75
	EtI	$10Et_2O$	85
NaMgPb	EtCl	—	20
	EtCl	$5Et_2O$	75
(NaK)Pb[c]	EtCl	—	25
	EtCl	$0.2CH_3COCH_3$	>95

[a] Atom % Al, based on Na in alloy.
[b] Atom % I_2, based on Pb in alloy.
[c] Equiatomic proportions of lead and alkali metals, in which 15 atom % of the alkali metal is K.

Discussion

It is clear from the reactions described herein, that there is a large variety of possible reactions of lead metal or alloys to form tetraalkyllead compounds from alkyl halides. This choice encompasses a considerable degree of diversity in the form of the metallic lead, the whole gamut of reducing metals in their many permutations and combinations, including intermetallic compounds of lead; the variation in types of alkyl halides, the choice of organometallic reagents and the manifold possible catalyst and solvent systems. The reactivity of the different metal–alkyl halide systems varies widely. The reactivity evidently depends upon: the nature of the surface and the porosity of the lead metal; the lattice structure, crystal size, and thermal history of the alloy; the accelerators or poisons present in the heterogeneous system and the molecu-

lar dimensions of the alkyl halide, as well as on the chemical activity of the metal and halide atoms.

Many inert systems, such as the system sodium-lead–methyl chloride, respond rapidly to the addition of catalysts. Despite the significant exception of the sodium-lead–methyl chloride system, it appears that methyl compounds react better than ethyl compounds. In general, iodides are superior to bromides and to chlorides as alkylating agents. If iodine were a relatively inexpensive element, it would probably be used for the commercial manufacture of tetraethyllead.

The mechanism of the reactions described above is as yet unknown. Unpublished evidence (*3*) has been obtained that a layer of alkyl halide is adsorbed onto the lead surface, and this is evidently the first step in the reaction. Beyond this, factual information is as yet unavailable. Correspondingly, there is an unpredictably wide variation in the yields of the tetraalkyllead product.

Patently, in the preparation of tetraethyllead there are many possible ways to reduce the recycling of lead metal, to replace sodium by other metals or to eliminate it, and to obtain more tetraethyllead per autoclave charge per unit time. The reaction of monosodium-lead alloy with ethyl chloride as it is carried out today is unique in its combination of favorable characteristics. Other reactions that have been proposed as replacements carry such liabilities as higher temperature, recovery problems, catalyst problems, lower yield with reducing metal, more expensive halide, etc., factors which detract from their commercial attractiveness.

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Several of the author's colleagues at the laboratories of the Ethyl Corp. have cooperated in the experimentation reviewed in this paper. To these people thanks are due.

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A New Method for the Synthesis of Tetraethyllead

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It was discovered that successful reactions could be obtained between a wide variety of organometallic compounds and lead sulfide, lead oxide, and the lead salts of inorganic or organic oxy- and thioacids. Even mixed compounds of lead oxide and the lead salts of the organic oxyacids undergo reaction to form tetraethyllead. In particular, organometallic compounds of elements in Groups IA, IIA, IIIA, and IIB as well as the complex organometallic compounds derived from the elements in these groups, such as lithium tetraethylaluminum, are effective in reactions with nonhalide lead compounds of these types. Tetraorganolead yields vary with reaction conditions, reactants, and solvents used. Temperature conditions required to initiate reactions are mild and in some cases are as low as −24°C. Rates of reaction are moderate to rapid, depending on the reaction conditions. Solvents are desirable to improve either reaction control and/or contact between reactants when one or both are solids under normal conditions. Solvents which have been used successfully in these reactions include hydrocarbons, amines, ethers, esters, and chlorinated hydrocarbons. It is the aim of this paper to cite a number of examples, so that the reader can appreciate the broad scope of the reaction of organometallic compounds with nonhalide lead compounds.

In recent years Ethyl Corp.'s research chemists have discovered a number of interesting new reactions in their exploration of new methods of synthesizing organolead compounds and, in particular, tetraethyllead Another paper (*15*) describes several of these methods in which the ethylating agents are ethyl esters of inorganic or organic acids and the lead-containing reactants are alloys of lead or lead metal itself. This paper describes some other methods in which the ethylating agents are organometallic compounds and the lead containing reactants are lead sulfide, lead oxides, or lead salts of inorganic or organic oxy- and thioacids.

Presented here is a brief account of some of the research work done in this field to date. Because of time limitations, many of the details are omitted and the exam-

ples are restricted to the preparation of tetraethyllead. It is intended to publish, at some future date, additional papers which will treat in greater detail each of the major phases of the work herein described.

Historical

The first successful synthesis of tetraethyllead is generally ascribed to Löwig (*9*) who, in 1853, obtained this compound from the reaction of ethyl iodide with sodium-lead alloys containing 16 to 25% sodium. The present commercial method for tetraethyllead manufacture is a modification of Löwig's discovery as described in a patent issued to Kraus and Callis (*7*) in 1926.

Closely following Löwig's work was that of Buckton (*1*) who, in 1859, reported the synthesis of tetraethyllead by reaction of diethylzinc and lead chloride. This is the first example of the preparation of tetraethyllead by reaction of an organometallic compound with a lead salt. Since that time, a number of publications have appeared dealing with the synthesis of tetraorganolead compounds by reactions analogous to that which Buckton discovered. These are summarized by Jones and Gilman (*6*) and Leeper, Summers, and Gilman (*8*) and for that reason are omitted here. However, with one exception, the lead salts used were all halides. The one exception is reported by Nad and Kocheshkov (*11*) on the formation of diaryllead acetates by reactions of diarylmercury compounds with lead acetate in chloroform solution. The products of these reactions are only partially arylated, however, and still retain saltlike properties. Thus, the literature contains no reference to the formation of tetraorganolead compounds by reaction of an organometallic compound with lead compounds other than lead halides.

A considerable area of ignorance has existed regarding the potential reactivity of many other lead compounds toward organometallic compounds in the synthesis of tetraorganolead products. Ethyl Corp.'s chemists explored the field of lead compounds experimentally, so as to include (1) lead sulfide, (2) the oxides of lead, (3) the lead salts of inorganic and organic thio- and oxyacids, and (4) the mixed compounds of lead oxide with the lead salts of organic oxyacids.

Reactions of Organometallic Compounds with Sulfide and Oxides of Lead

Probably the most significant discovery discussed in this paper is that lead sulfide, lead oxide, and lead dioxide react with organometallic compounds to form tetraethyllead. For the most part, the organometallic compounds are derived from elements in Groups IA, IIA, IIIA, and IIB of the periodic table. Considering the inertness of these lead compounds, it was somewhat surprising to find that they participated in these reactions. Even more unexpected was the fact that the primary organolead product of these reactions was completely ethylated.

Table I. Tetraethyllead Yields from Reactions with Lead Sulfide

EtM[a]	Mole Ratio EtM[a]/PbS	Solvent	EtM[a] Concn., Moles/L.	Reaction Conditions: Time, hr.	Reaction Conditions: Temp., °C.	Yield, %[b]
C_2H_5Li	4.9	Diethyl ether	0.43	2.5	35	15
$C_2H_5Li + C_2H_5Na$	1.1		0.10	4.5	25	81
C_2H_5MgBr	3.4	Toluene	0.87	3.5	110	6
$(C_2H_5)_2Mg$	1.0	Diethyl ether	0.15	3.0	35	42
$(C_2H_5)_2Zn$	4.0	Toluene	7.7	3.5	110	53
$NaZn(C_2H_5)_3$	3.0	Dimethyl ether	0.97	9.0	−24	30
$(C_2H_5)_3Al$	3.1	Toluene	0.37	1.5	110	65
$LiAl(C_2H_5)_4$	1.0	Hexane	0.09	4.2	120[c]	38
$NaAl(C_2H_5)_4$	3.3	Toluene	0.70	1.0	110	66

[a] EtM = organometallic compound.
[b] Based on 50% theoretical conversion of lead in sulfide to $(C_2H_5)_4Pb$. Example: $4C_2H_5Li + 2PbS \rightarrow (C_2H_5)_4Pb + 2Li_2S + Pb$.
[c] Reaction conducted under pressure.

Shown in Table I are some examples of results obtained in reactions of typical organometallic compounds derived from elements in Groups IA, IIA, IIIA, and IIB with lead sulfide. Both the simple and complex organometallic compounds react with lead sulfide to form tetraethyllead.

The highest yield cited (81%) is for the reaction of a mixture of ethyllithium and ethylsodium [prepared according to Wittig's method for sodium diphenyllithium (*17*)] with lead sulfide in diethyl ether using an organometallic–lead sulfide mole ratio of 1 to 1. This example is instructive in showing the mild conditions under which these reactions proceed. The 81% yield was obtained in 4.5 hours at 25°C. Possibly more striking proof of the ease with which these reactions proceed is the example of zinc triethylsodium which gave a 30% yield in reaction with lead sulfide at −24°C. in 9 hours.

The other examples presented show the variety of organometallic compounds which react with lead sulfide to form tetraethyllead. Moderately high yields were obtained for the conditions used with sodium tetraethylaluminum (66%), triethylaluminum (65%), and diethylzinc (53%). Lower yields were obtained with the other organometallic compounds under the reaction conditions cited.

In Table II are presented similar data for reactions of organometallic compounds

Table II. Tetraethyllead Yields from Reactions with Oxides of Lead

Oxide of Lead	EtM[a]	Mole Ratio EtM[a]/Oxide	Solvent	EtM[a] Concn., Mole/L.	Reaction Conditions Time, hr.	Temp., °C.	Yield, %[b]
PbO	C_2H_5Li	3.0	Diethyl ether	0.19	3.0	125[c]	64
	C_2H_5MgBr	2.4	Hexane	0.28	3.0	120[c]	13
	$(C_2H_5)_2Mg$	2.0	Diethyl ether	0.15	6.0	35	18
	$(C_2H_5)_2Zn$	0.5	Toluene	0.19	4.5	110	47
	$(C_2H_5)_3Al$	0.7		0.70	2.5	110	63
	$LiAl(C_2H_5)_4$	1.8	Hexane	0.16	2.0	130[c]	64
	$NaAl(C_2H_5)_4$	0.5	Toluene	0.70	1.0	110	3
PbO_2	$(C_2H_5)_3Al$	1.3	None	—	2.0	105	19[d]

[a] EtM = organometallic compound.
[b] Based on 50% theoretical conversion of lead to $(C_2H_5)_4Pb$.
[c] Conducted under pressure.
[d] Based on 100% theoretical conversion of lead in PbO_2 to $(C_2H_5)_4Pb$. $3PbO_2 + 4(C_2H_5)_3Al \rightarrow 3(C_2H_5)_4Pb + 2Al_2O_3$.

with lead oxide and a single reaction of triethylaluminum with lead dioxide. With the exception of the reaction of diethylmagnesium and lead oxide, all the other reactions were carried out above 100°C. in the examples presented. Reasonably high yields were obtained with lithium tetraethylaluminum (64%), ethyllithium (64%), and triethylaluminum (63%). Diethylzinc gave a moderately high yield (47%) and smaller yields were obtained with the other organometallic compounds.

The example of the reaction of lead dioxide with triethylaluminum shown in Table II was carried out in the absence of solvent. A yield of 19% tetraethyllead was obtained in 2 hours at a temperature of 105°C.

Organometallic compounds which are normally liquids, such as triethylaluminum or diethylzinc, may be reacted in the absence of solvent with lead sulfide and the lead oxides. However, some care must be exercised under these conditions to avoid rapid heat generation and even violent reaction. The use of solvents permits better reaction control through improved heat removal and agitation. When the organometallic compounds are normally solids, solvents are desirable for the reasons stated above and also to solubilize the reactants, to permit more rapid reaction through improved contact.

Reaction of Lead Salts of Inorganic Acids

A number of reactant combinations of organometallic compounds and lead salts of inorganic oxy- and thioacids were also found to produce tetraorganolead compounds.

For purposes of brevity, however, the reactions of only three lead salts with triethylaluminum are presented to illustrate the results obtained.

Table III. Tetraethyllead Yields from Reactions of Triethylaluminum with Lead Salts of Inorganic Acids

Lead Salt	Mole Ratio Et_3Al^a/Salt	Solvent	Et_3Al^a Concn., Mole/L.	Reaction Conditions Time, hr.	Temp., °C.	Yield,[b] %
$PbSO_4$	1.4	Toluene	0.7	1	110	54
$Pb(NO_3)_2$	0.61	Ethylene glycol dimethyl ether	0.9	1	85	50
$Pb(SCN)_2$	0.66	Toluene	0.5	3	110	39

[a] Et_3Al = triethylaluminum.
[b] Based on 50% theoretical conversion of lead to tetraethyllead.

As shown in Table III, lead sulfate and nitrate gave 54 and 50% yields, respectively, under the conditions tested. Lead thiocyanate reacted to give a 39% yield of tetraethyllead. Similar results were obtained with other lead salts in this class, such as lead borate and lead carbonate.

For the examples shown, toluene or ethylene glycol dimethyl ether solvents were satisfactory. Reaction temperatures at about the boiling point of the solvents were adequate to give the stated yields in 1 to 3 hours' reaction time.

A rather striking color change occurs during reaction. The lead salts tested are white, but promptly on initiation of the reaction the surface of the salt particles turns dark and then black. This is due to the formation of metallic lead during the reaction which is deposited on the surface of the salt particles. In many cases, this change occurs almost instantaneously when the organometallic compound is brought into contact with the lead salt. This observation illustrates the high degree of reactivity of the organometallic compounds with lead compounds of the type discussed in this paper.

Reactions with Lead Salts of Organic Acids

A number of lead salts of organic acids were tested with various organometallic compounds, particularly those of elements in Groups IA, IIA, IIIA, and IIB. In all cases successful reactions with the formation of tetraorganolead compounds occurred.

Reactions with lead salts of this type are characterized by rapid reaction rates and high yields. This is particularly true for those lead salts or organic acids which have a moderate or high solubility in the solvents. Completely homogeneous reactions are possible with some lead salts and the organometallic compounds by selection of the proper solvents. Under such conditions, maximum reaction rates are possible. The potential of such reactions will be more evident as specific examples are discussed.

A number of examples of reactions with lead salts of organic acids are presented in Tables IV, V, and VI. In Table IV are shown two examples with lead formate, the salt of the simplest organic acid. For the examples shown, diethylzinc in toluene reacted almost quantitatively (95% yield) based on the amount of diethylzinc used, to form tetraethyllead. The reaction was conducted at 111°C. for 1.5 hours. Tri-

Table IV. Tetraethyllead Yields from Reactions with Lead Formate

EtM^a	Mole Ratio EtM^a/Salt	Solvent	EtM^a Concn., Mole/L.	Reaction Conditions Time, hr.	Temp., °C.	Yield,[b] %
$(C_2H_5)_2Zn$	0.73	Toluene	0.70	1.5	111	95
$(C_2H_5)_3Al$	0.45	Diethylene glycol dimethyl ether	0.70	1.5	100–110	73

[a] EtM = organometallic compound.
[b] Based on 50% theoretical conversion of lead to tetraethyllead.

Table V. Tetraethyllead Yields from Reactions with Lead Acetate

EtM[a]	Mole Ratio EtM[a]/Salt	Solvent	EtM[a] Concn., Mole/L.	Reaction Conditions Time, hr.	Temp., °C.	Yield,[b] %
$(C_2H_5)Na$	1.67	Heptane	1.0	1.7	60	100
$(C_2H_5)_2Mg$	0.91	Ethylene glycol dimethyl ether	0.34	2	60–100	76
$(C_2H_5)_2Zn$	1.0	Toluene	0.70	1	111	93
$(C_2H_5)_3Al$	0.61	Diethylene glycol dimethyl ether	0.70	0.5	room temp.	97
	0.61	Tetrahydrofuran	0.73	1.5	66	96
$NaAl(C_2H_5)_4$	0.50	Toluene	0.70	3	111	73

[a] EtM = organometallic compound.
[b] Based on 50% theoretical conversion of lead to tetraethyllead.

Table VI. Tetraethyllead Yields from Reaction of Triethylaluminum with Other Lead Salts of Organic Acids

Lead Salt	Mole Ratio Et_3Al[a]/Salt	Solvent	Et_3Al[a] Concn., Mole/L.	Reaction Conditions Time, hr.	Temp., °C.	Yield, %
Lead tetraacetate	1.0	Toluene	0.35	2.5	0–10	65[b]
Lead stearate	0.71		0.35	0.5	111	81[c]
Lead oxalate	0.66		0.49	3.0	111	18
Lead naphthenate[d]	0.54	Ethylene glycol dimethyl ether	0.70	0.25	room temp.	91
Lead linoresinate[e]	1.0		0.70	1.0	111	94

[a] Et_3Al = triethylaluminum.
[b] Based on 100% theoretical conversion of lead to tetraethyllead.
[c] All others based on 50% theoretical conversion of lead to tetraethyllead.
[d] Naphthenic acid is a mixture of cycloparaffinic acids.
[e] Derived from tall oil which contains resin and fatty acids.

ethylaluminum in diethylene glycol dimethyl ether gave a 73% yield under essentially the same conditions of reaction time and temperature.

In Table V are shown other examples of reactions of organometallic compounds with lead acetate, the salt of another simple organic acid. Outstanding is the quantitative yield obtained with ethylsodium in heptane. In this particular reaction, excess ethylsodium was used to give theoretical (50%) conversion of the lead in lead acetate to tetraethyllead. Near quantitative yields were obtained in reactions of triethylaluminum (97%) and diethylzinc (94%), respectively, with lead acetate. With triethylaluminum, the lead acetate was in excess and with diethylzinc the reactants were present in equimolar (theoretical) quantities. In both of these cases the reaction times were short. Striking is the 97% yield obtained with triethylaluminum in ½ hour at room temperature. This illustrates the fast reaction rates and high yields obtainable in these actions under very mild conditions. The other examples (diethylmagnesium and sodium tetraethylaluminum) gave poorer yields under the conditions cited.

In Table VI are shown examples of reactions of triethylaluminum with lead salts of more complex organic acids including oxalic, stearic, naphthenic acids, and acids derived from tall oil. In addition, an example of a quadrivalent lead salt is given to complete this general class of lead salts of organic acids.

Lead tetraacetate, using an excess of triethylaluminum, gave a 65% yield of tetraethyllead at 0° to 10°C. in 2.5 hours' reaction time. This also represents a 65% conversion of lead in this salt to tetraethyllead, which indicates that the potential conversion of lead in this quadrivalent lead salt is 100%.

The lead salts of acids derived from tall oil, naphthenic, and stearic acids gave high yields under the conditions tested (94, 91, and 81%, respectively). The 91% yield obtained with lead naphthenate in ¼ hour and the 81% yield obtained with lead stearate in ½ hour again illustrate the rapid reaction rates possible. Reactions such as these are homogeneous, because the organometallic compounds as well as the lead salt are soluble. In the case of lead naphthenate, which is completely soluble in the solvent, the rapid reaction and high yield were obtained at room temperature.

Reactions with Mixed Compounds of Lead Oxide and Lead Salts of Organic Acids

Lead oxide forms mixed compounds with lead salts of organic acids. Because lead oxide and the lead salts independently react with organometallic compounds, it was of interest to determine whether the mixed compounds would also react to form tetraethyllead.

In all cases tested, these materials reacted to form tetraethyllead. Some examples are shown in Table VII. Lead formate–lead oxide (1 to 1 mole ratio) gave a 50% yield. Three mixed compounds of lead oxide and lead acetate were tested in which the oxide-salt mole ratios were 1 to 1, 2 to 1, and 5 to 1. The yields decreased progressively from 70% to 25% as the ratio increased. The same trend was observed for the lead oxide–lead stearate series though the yield drop corresponding to the highest lead oxide–containing mixed compound was less severe than for the acetate series.

Table VII. Tetraethyllead Yields from Reactions with Triethylaluminum with Mixed Compounds of Lead Oxide and Lead Salts of Organic Acids

Lead Salt	Mole Ratio PbO/Salt	Mole Ratio Et_3Al[a]/Mixed Compound	Solvent	Et_3Al[a] Concn., Mole/L.	Reaction Conditions: Time, hr.	Temp., °C.	Yield,[b] %
Formate	1 to 1	1.3	Ethylene glycol dimethyl ether	0.70	1.5	85	50
Acetate	1 to 1	1.3		0.70	1	85	70
	2 to 1	1.9	Toluene	0.30	3	111	38
	5 to 1	4.0		0.30	3	111	25
Stearate	1 to 1	1.2	Ethylene glycol dimethyl ether	0.70	1	85	80
	3 to 1	2.2		0.70	1.5	85	55
	5 to 1	3.1		0.35	3	85	53

[a] Et_3Al = triethylaluminum.
[b] Based on 50% theoretical conversion of lead to tetraethyllead.

These and related data suggest that the mixed salts tend to react as a mixture of the two components. Further work is necessary to clarify these relationships.

Experimental

Most reactions discussed in this publication were carried out in glassware reactors fitted with agitator, condenser, thermometer, and stoppered openings for the introduction of reagents. In general, the anhydrous lead compound and solvent were introduced into the reaction flask which had been purged with dry nitrogen. After the reactor contents had been brought to the desired reaction temperature, the organometallic compound was added to this anhydrous environment. When the stated reaction period was ended, the mass was allowed to cool and the residual organometallic compound destroyed with isopropyl alcohol and water. The organic layer was then analyzed for tetraethyllead.

The various organometallic compounds used in this work were prepared by reliable procedures reported in the literature. The Grignard reagents (*12*) were used in ethyl ether solution as prepared. This was also true of the ethyllithium used (*3*). Triethylaluminum and its derivatives were prepared ether-free by reported procedures (*4*). Diethylmagnesium was prepared from the Grignard reagent (bromide) by the dioxane precipitation method (*14*). Diethylzinc was synthesized from ethyl iodide and zinc metal powder by the usual procedure (*10*). Ethylsodium was synthesized from diethylmercury and sodium (*13*).

Reagent grade lead compounds were used in all cases. These materials were vacuum dried or dried by azeotropic distillation. Lead naphthenate was obtained from Advance Solvents Co. and the lead salt of tall oil from the Harshaw Chemical Co.

Reagent grade or high grade commercial solvents were used, depending on availability. These materials were dried over sodium wire and used without further purification.

Two different analytical methods were used to determine the tetraethyllead formed. The dithizone method (*16*) was used when low yields were obtained; for substantial yields, the iodometric (*5*) method was employed. In many cases, the tetraethyllead was isolated from the reaction mass by vacuum distillation and identified by its physical properties.

Yields were calculated, for all reactions cited in this paper, on the basis of the valency of the lead compound used. It was assumed that the maximum possible conversion of lead in the divalent compound was 50% as given by the example:

$$4C_2H_5Li + 2PbO \rightarrow (C_2H_5)_4Pb + Pb + 2Li_2O$$

This is consistent with the known stoichiometry of the reaction with the divalent halides (*2*). In the case of lead dioxide and lead tetraacetate, the yield was based on the assumption that the maximum possible conversion of lead in these quadrivalent compounds was 100%.

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Chemical Reactions of Tetraethyllead

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This report gives a compilation of the periodical and patent literature on the known chemical reactions of tetraethyllead (TEL). These are by no means confined to antioxidant and antiknock effects. Of particular interest are those reactions wherein ethyl radicals, liberated from TEL by photolysis or pyrolysis, induce the polymerization, chlorination, or oxidation of other compounds. Many different diethyl- and triethyllead salts are readily obtained from the parent compound. TEL is used to prepare other organometallic compounds, and its reaction with heavy metal chlorides produces Ziegler-type catalysts for the polymerization of olefins. In view of its ready availability, these relatively unexplored end uses for TEL constitute an area of considerable research potential.

Tetraethyllead—commonly abbreviated to TEL—is the outstanding example of the simple or R_nM type of organometallic compound of moderate chemical reactivity. It has been known for over 100 years, as it was one of the first of these compounds to be isolated, and it is now unique in industrial importance. As a consequence, the reactions of TEL have been widely investigated. However, there still remain many opportunities for worthwhile research in this field.

The chemistry of organolead compounds in general has often been reviewed (*58, 113, 120*), notably by Calingaert (*17*), Krause (*82*), and most recently Gilman (*45, 83*) and their coworkers: men who have contributed much of the important experimental work on the subject. Reviews in particular have been made by German and Russian workers (*81, 131*), but these are not readily accessible and are now out of date.

Considering the variety of chemical reactions into which TEL can enter, and its ready availability at a relatively low cost, there may well be good use for the following compilation of the available information on these reactions.

Photolysis

TEL is readily dissociated by light. The vapor shows continuous absorption in the ultraviolet with the formation of metallic lead and ethyl radicals, the latter being detected by the Paneth method (*33, 103, 124*). Maximum absorption occurs at about

λ2000, but the limit for either the vapor or liquid solutions is around λ3500 (*85*) and pure TEL is slightly sensitive even to diffuse daylight.

In the liquid phase, the dissociation likewise may yield metallic lead, but as a rule the presence of dissolved air or carbon dioxide and water causes the appearance of a white haze and subsequent precipitation of unidentified products (*85*).

The quantum yield in the photolysis of the vapor or of dilute solutions is evidently about unity or less (*85*); for pure liquid TEL, it has not been measured. As would be expected, the dissociation in solutions is greatly reduced by screening agents such as dyes (*108*).

Pyrolysis

TEL is very stable at room temperature, but on heating it undergoes an exothermic dissociation, giving a complex of reaction products.

Liquid TEL dissociates at a rate reported to be about 2% per hour at 100°C. (*18*), while at 200°C. the dissociation is complete in perhaps a minute. This is evidently a chain reaction, since it can be suppressed for a long period of time—e.g., for over 10 hours at 130°C.—by the addition of as little as 0.01% of an effective stabilizer such as styrene or naphthalene (*18*) or by dilution with an inert solvent. The reaction liberates gases and is highly exothermic, and the heat of reaction increases markedly with temperature. Thus in handling bulk quantities precaution has to be taken to avoid local overheating with resulting development of very rapid decomposition (*18*). The reaction products, in addition to metallic lead, are principally ethane and ethylene together with some butane and butylene and minor amounts of higher paraffins and olefins (*94*). The proportion of these heavier hydrocarbon products will increase with the temperature at which the dissociation occurs, thereby increasing the heat of the reaction.

No detailed study of the reaction mechanism has been made, but it is evidently complex. The initial process is presumably the formation of an ethyl radical and a triethyllead radical. Reaction of the ethyl radical with TEL could yield the observed ethane, ethylene, and butane, together with triethyllead. However, it is not clear how this latter radical continues the chain: The formation and subsequent reaction of hexaethyldilead would not be expected to yield free ethyl (*88*). It may be that the triethyllead quickly dissociates to diethyllead, regenerating the ethyl radical.

TEL vapor is far more stable than the liquid, and its dissociation has been investigated in some detail. Paneth (*99*), and later Pearson (*100*), and their coworkers showed that mirrors of zinc, cadmium, arsenic, antimony, and lead are removed by the ethyl radicals formed on pyrolysis of dilute TEL vapor in hydrogen. At temperatures from 245° to 275°C. and pressures of 13 to 52 mm., Leermakers (*84*) found that the dissociation of the vapor is nearly homogeneous and first-order, with a velocity constant of $k = 1.2 \times 10^{12}\, e^{-36900/RT}$ sec.$^{-1}$; the rate is not affected by the presence of azomethane or hydrogen. Using the flow method, at 500°C. and 0.5-mm. pressure Meinert (*94*) obtained complete dissociation in a few tenths of a second, which is about what would be expected, but at atmospheric pressure and temperatures from 300° to 475°C. his data indicate rates considerably lower than predicted by the above relation.

The reaction products of the vapor phase dissociation are distinctly different from those obtained in the liquid phase. Hydrogen appears in quantity and the amount of butane is much greater (*44*, *94*, *99*). Using both static and flow methods over a wide range of conditions, Meinert (*94*) concluded that the products result largely from reactions of ethyl radicals at the walls, either with TEL to form ethane or with one another to form butane or ethylene and hydrogen; the gas phase reaction of two ethyl radicals to give ethane plus ethylene occurs to a lesser extent.

In none of these investigations is there any information as to the history of the lead atom prior to its ultimate appearance as metallic lead. As mentioned above, the initial product is presumably a triethyllead radical. This should be much more stable

than the ethyl radical, but it may simply dissociate further before it has an opportunity to react otherwise. Experiments on the pyrolysis of mixed R_4Pb compounds might throw light on this subject.

A process for coating iron with lead by pyrolysis of TEL is described in an early patent (*70*). For the most part, however, the dissociation is used as a source of ethyl radicals to promote polymerizations or other reactions.

Polymerization of Olefins and Other Compounds

The liberation of free ethyl and alkyllead radicals in the dissociation of TEL offers attractive possibilities for using these to promote other chemical reactions.

Even before Paneth's demonstration (*99*) of the free ethyl radical, Taylor and Jones (*123*) showed that dissociation of TEL vapor at 250° to 350°C. induces polymerization of ethylene gas to a high-boiling liquid. Subsequently, Cramer (*29*) heated a 28 volume % solution of TEL in benzene in an autoclave at about 200° to 250°C. and 70 atm., and obtained principally ethane and a light polyethylene oil; the benzene was inert, as was added hydrogen. When an additional amount of ethylene was added at the start, most of it also polymerized, even though the amount of TEL was reduced to only 0.2%. Dissociation of TEL in naphthalene is like that in benzene, there being no detectable reaction with the solvent (*30*). This is remarkable in view of the effectiveness of naphthalene as a stabilizer in the decomposition at lower temperatures (*18*). In the similar high-temperature dissociation of TEL in paraffinic, naphthenic, or olefinic solvents, the ethyl radicals attack the solvent, abstracting hydrogen to form ethane or alkylating the double bond, and yielding light colored oils (*30, 31*).

Propylene is much less readily polymerized by ethyl radicals from TEL than is ethylene, both at 1 atm. and 400°C. (*7*) and at 250 atm. and 300°C. (*128*). Even under the latter condition, no more than 480 moles of propylene are polymerized per mole of TEL, and much of the product is of low molecular weight, whereas ethylene gives largely an oil boiling above 200°C. at 15 mm. (*80*). At atmospheric pressure, the yields and molecular weights of the polymers are very low for both ethylene and propylene (*7*).

These are the only disclosures which include patent claims of TEL as a promoter for the polymerization of ethylene, although there are a number of patents which list TEL along with other known compounds for this use. Examples refer to ethylene alone (*109*) or in solution (*111*) or in telomerization reactions (*110, 115*). TEL is specifically claimed, however, as one of the promoters for the telomerization of ethylene with hydrogen chloride: At 50° to 150°C. and 400 to 1000 atm. this reaction yields a mixture of alkyl chlorides of which a large part is grease and wax of molecular weight about 400 (*60*). There are fewer patent references to the use of TEL for the polymerization of heavier olefins such as, for example, butadiene and butadiene-styrene mixtures (*39*).

Another reaction of the ethyl radical from TEL is the abstraction of hydrogen from an arylalkane or from triptane to form ethane, after which the resulting radical dimerizes—for example, toluene gives bibenzyl (*125*). This is effected at 250°C., or in sunlight at room temperature.

Relatively little has been accomplished in the TEL-promoted polymerization of compounds other than olefins, although an early (1930) patent (*136*) specifies and claims TEL for use with vinyl chloride and vinyl acetate. It is noteworthy that the temperature specified in this case is only 80° or 100°C. 3-Chloro-2-methylpropene in solution with TEL is dimerized when the TEL is dissociated by exposure to light (*133*). One group of patents (*105, 132*) describes the production of vinylidene chloride polymers or copolymers by the use of TEL in conjunction with benzoyl peroxide and a polychloro compound and copper.

TEL has been proposed as an initiator for the polymerization of dehydrogenated

rosin derivatives, including acids, esters, alcohols, and rosin oil (*10*). Polymerization is effected over the temperature range of 200° to 250°C. Rubber compounds have been treated with TEL for the purpose of hardening: Reinforcing compounds are claimed to be produced in place by decomposition of the TEL (*127*).

The chlorination of certain hydrocarbons catalyzed by TEL has been comprehensively studied by Vaughan and Rust (*129, 130*). These hydrocarbons include ethane, propane, and cyclopentane in the vapor phase, and *n*-pentane in the liquid phase. All chlorinations were conducted in the dark. Small amounts of TEL (0.002 mole %) in mixture with chlorine and ethane result in complete reaction of chlorine at 120°C. The product obtained consists of 80 mole % ethyl chloride and 20 mole % higher chlorides, the same distribution as in the high-temperature thermal reaction. Under the above conditions, however, no reaction at all occurs in the absence of TEL. Similar reactions have been carried out with propane at 136° to 140°C., cyclopentane at 135°C., and *n*-pentane at 10°C. The authors assume that the chlorination is initiated by highly reactive species, such as an ethyl radical formed during the reaction of the chlorine and TEL. The mechanism whereby such a radical is liberated in this process is not evident.

Tetraethyllead has been patented as a free radical initiator for the addition of hydrogen bromide, hydrogen sulfide, and mercaptans to propylene (*38*), forming the normal propyl derivative (contrary to Markownikoff's rule). The TEL is dissociated by the action of ultraviolet light to ethyl radicals which initiate the abnormal addition of temperatures not in excess of 25°C.

When TEL is added to cupric nitrate in an alcoholic solution containing styrene, methyl methacrylate, or acrylonitrile, there is rapid polymerization of the unsaturated compound at room temperature (*6*). With silver nitrate in place of the copper salt, this does not occur. It appears, therefore, that this polymerization is not a free radical process, but that the initiation is probably determined by a redox system involving copper ions.

A recent patent (*95*) states that TEL may be substituted for aluminum, magnesium, or zinc alkyls in preparing Ziegler-type catalysts for the polymerization of α-olefins. Specifically, the catalyst is prepared by reacting TEL with halides of the transition metals of groups IV to VIII of the periodic table. Examples of these are titanium tetrachloride and molybdenum and vanadium pentachlorides. The polymerization reaction is carried out in a paraffinic solvent at a temperature of 90° to 180°C. and ordinary or elevated pressures. This method gives a crystalline polyethylene in an amount 50 times that of the TEL used.

A patent has been issued on the use of TEL as a condensation catalyst to form polyester resins, such as may be obtained from methyl terephthalate and glycol (*16*). In an example, 0.03% TEL based on the weight of methyl terephthalate is used. The reaction rate is claimed to be two to five times that given by conventional catalysts. Emphasis is placed on the stability of the alkyllead compound at the high temperatures employed, and on the avoidance of water and free acid. The nature of the actual catalyst in this case is not at all evident, and further investigation along this line would be of interest.

Reaction with Hydrogen

The dissociation of TEL by hydrogen to give ethane and metallic lead has been studied under noncatalytic conditions (*71, 72*) at temperatures from 100° to 225°C. and with initial pressures of hydrogen of some 60 atm. In benzene solutions, using a reaction period of 24 hours, 15% of the lead is liberated at 100°C., 50% at 175°C., and 99% at 225°C. Apparently, the catalytic hydrogenation of TEL has not been studied. However, the nickel-catalyzed hydrogenation of tetra-*n*-heptyllead gives at least a 62% yield of the R-R product, tetradecane (*137*).

Oxidation and Antioxidant Action

Liquid TEL oxidizes in air, very slowly at room temperature and rapidly at temperatures over 100°C. The vapor is much more resistant to oxidation than the liquid, at a given temperature. However, there has been no publication of the nature and products of the oxidation, or of the effects of catalysts, inhibitors, etc.

Strong oxidizing agents such as potassium permanganate, sulfuryl chloride, and calcium hypochlorite effect complete decomposition of TEL at low temperature. These reagents are the ones used in industry for decontamination of TEL spills and for final cleaning of equipment contaminated with TEL or its partial-decomposition products. The toxicity of TEL and other organolead compounds and their insidiousness (for they are in no sense self-warning) make it mandatory to use adequate precautions in handling. In decontamination, care must be taken to use the above oxidants in sufficient excess to accomplish complete decomposition of TEL, and in adequate dilution in appropriate solvents so as to control the speed of the reaction, which otherwise may be violent. TEL in a dilute solution—e.g., in gasoline—is oxidized at low temperature by nitrogen dioxide, forming diethyllead dinitrate which is readily separated from the solvent (*107*).

A further example of the oxidizability of TEL is afforded by a patent on mixtures of TEL and tetranitromethane as an explosive of unusual strength and high rate of detonation (*134*). On the other hand, another patent states that addition of a small amount (about 1%) of TEL lowers the burning rate of a mixture of tetranitromethane with 10 to 20% of benzene to the point where this can be successfully used as a propellant (*61*). These two results are not discordant: In the former case, TEL serves as a fuel having a high heat of combustion per unit volume; in the latter case it evidently exerts its characteristic antioxidant action.

This antioxidant action of TEL was at once suspected when its antiknock effect became known. Soon thereafter, Moureau and Dufraisse (*96*) reported that TEL is an antioxidant for benzaldehyde at room temperature, and numerous investigators observed its inhibitory effect in the slow oxidation of hydrocarbons at elevated temperatures (*92*). Since that time there has been a great deal of work carried out which involved these antiknock and antioxidant effects. However, there has been no study of the mechanism and products of the reactions which the TEL itself undergoes in exerting these effects.

Under certain circumstances, TEL may also act as a promoter of oxidation reactions, presumably by supplying free radicals. For example, in a hydrocarbon reference fuel, a very high concentration of TEL (far beyond the range of normal usage) actually has a proknock effect. In the liquid phase oxidation of alkylbenzenes catalyzed by a metal oxide or salt, addition of TEL is claimed to increase the yield of toluic acids (*66*).

Reaction with Halogens

The reaction of TEL has been studied with chlorine, bromine, and iodine. There are no literature reports on the behavior of TEL with elemental fluorine. The reaction of halogens with TEL involves cleavage of the lead-carbon bond, and the initial products are dependent upon the reaction temperatures and amounts of halogen employed (*59*). With chlorine, the reaction may be indicated by the steps:

$$Et_4Pb \xrightarrow{-60^\circ} Et_3PbCl \xrightarrow{-10^\circ} Et_2PbCl_2 \rightarrow EtPbCl_3 \rightarrow PbCl_2 + EtCl$$

At −60°C., the chlorination of TEL in ethyl acetate gives a quantitative yield of triethyllead chloride. Increasing the temperature to −10°C. after the initial chlorination at −60°C. and continuing the chlorination give a quantitative yield of diethyllead dichloride (*59*). Continuing the chlorination beyond that stage, by using more drastic

conditions, does not allow isolation of an ethyllead trichloride, because it is unstable and converts immediately to lead chloride and ethyl chloride.

Similar studies have been reported for bromine and iodine. Bromination of TEL in ether solution at −70°C. results in a quantitative yield of triethyllead bromide (*59*, *122*). In contrast to chlorination, however, the further bromination of TEL gives only low yields of the dibromide. Triethyllead iodide has been prepared in 73% yield by the reaction of TEL with iodine in ether solution at −60°C. (*23*, *78*, *86*).

The complete decomposition of TEL by bromine and chlorine, as indicated by the equations:

$$Et_4Pb + 3Br_2 \rightarrow PbBr_2 + 4EtBr \quad (28, 32, 36, 102)$$

$$Et_4Pb + 3Cl_2 \rightarrow PbCl_2 + 4EtCl \quad (114)$$

and the reaction with iodine:

$$Et_4Pb + I_2 \rightarrow Et_3PbI + EtI \quad (26, 36, 64)$$

have been the basis for several analytical procedures for TEL, since these reactions proceed quantitatively.

Reaction with Alkalies

Dilute and concentrated aqueous alkalies do not react with TEL at ordinary temperatures (*17*), while at high temperature apparently no study has been made. This inertness to alkali is probably not simply due to limited solubility, for it is believed that alcoholic potash is also unreactive. Moreover, TEL is inert to phenyllithium in ether solution at room temperature, in contrast to the moderately rapid exchange between tetraphenyllead and ethyllithium under the same conditions (*51*).

Reaction with Inorganic Acids

Studies of the reaction of TEL with halogen acids have been reported for hydrogen chloride and hydrogen bromide. The general equation for the reaction is:

$$Et_4Pb + HX \xrightarrow{\text{Solvent}} Et_3PbX + C_2H_6$$

Hydrogen chloride reacts with TEL at room temperature to give good yields of triethyllead chloride (*12*, *13*, *15*, *23*, *53*, *101*, *135*). A variety of solvents and gaseous or concentrated hydrogen chloride may be used. Use of the gas and a hexane solvent appears to be best on the basis of both yield (86 to 97%) and purity of product (*23*). Under more drastic conditions, the reaction may proceed beyond the triethyllead stage. Thus, in one study reported using toluene as a solvent and a temperature of 90°C., a mixture was obtained containing 50% lead chloride, 30% triethyllead chloride, and 20% diethyllead dichloride (*135*). Under even more rigorous conditions, lead chloride is the final product of the treatment with either hydrogen chloride gas or concentrated hydrochloric acid (*24*, *40*, *42*, *121*).

The reaction of TEL with hydrogen bromide proceeds in a similar manner. Using the gas with petroleum ether as a solvent, a yield of 84% of triethyllead bromide has been reported (*49*). The halogen acid may conveniently be provided in the form of an addition product with a trialkylamine, $R_3HNBr \cdot 2HBr$ (*76*).

There appears to be no published information on the reaction of TEL with hydrogen iodide or fluoride.

The di- and triethyllead halides conveniently serve as intermediates for the preparation of other di- and triethyllead salts by a metathesis (*23*, *45*, *83*).

Dilute nitric and sulfuric acids react with TEL only very slowly, if at all, at room temperature (*17*). However, on heating TEL with the dilute acids or on contact of it with concentrated acids at ordinary temperatures, an attack does take place. Thus,

heating TEL with 50% sulfuric acid leads to the formation of triethyllead sulfate and ethane (*17*). Concentrated nitric acid has been reported to decompose TEL completely to lead nitrate (*17, 74*); this can be a violent reaction. It has also been reported that TEL in chloroform solution reacts with concentrated nitric acid with the formation of diethyllead dinitrate and a small amount of triethyllead nitrate (*68*). When a vapor mixture of TEL and nitric acid is diluted with carbon dioxide and passed through a heated glass tube at 150°C., there is a complete conversion of the ethyl radicals to nitromethane and ethyl nitrate (*87*).

TEL has also been reported to react with concentrated phosphoric acid in the presence of silica gel to give triethyllead dihydrogen phosphate in a 26% yield (*54*).

Reaction with Organic Acids

The reaction of TEL with organic acids has been studied both in the presence and absence of silica gel. Generally speaking, reaction is greatly promoted by the presence of a small quantity of silica gel, although there are a number of anomalies. In some instances, no reaction at all is obtained either with or without silica gel; in other cases, complete dealkylation of TEL takes place. Table I summarizes the literature information on the subject.

Table I. Reaction of TEL with Organic Acids

Acid	Products	Yield, %	References
Acetic	Ethylene, ethane, ethyl acetate, lead acetate	—	(*73*)
Acetic[a]	Triethyllead salt	95	(*12, 54*)
Benzoic[a]	Diethyllead salt	—	(*63*)
Bromoacetic[a]	Triethyllead salt	—	(*12*)
m-Bromobenzoic[a]	Diethyllead salt Triethyllead salt	9.8 3.6	(*55*)
Butyric[a]	Triethyllead salt	—	(*12*)
d-Camphor-10-sulfonic[a]	Triethyllead salt	96.4	(*55*)
Chloroacetic[a]	Triethyllead salt	—	(*12*)
Cyanoacetic[a]	No reaction	—	(*55*)
Decanoic[a]	Not identified	—	(*12*)
Dibromoacetic[a]	Triethyllead salt	—	(*12*)
Dichloroacetic[a]	Triethyllead salt	—	(*12*)
Fluoroacetic[a]	Triethyllead salt	79.1	(*112*)
Formic[a]	Lead formate	—	(*55*)
Furanacrylic[a]	Triethyllead salt	—	(*54*)
Furoic[a]	Triethyllead salt	—	(*54*)
Heptanoic[a]	Triethyllead salt	—	(*12*)
Hexanoic[a]	Triethyllead salt	—	(*3, 12*)
Isobutyric[a]	Triethyllead salt	—	(*12*)
Isovaleric[a]	Triethyllead salt	—	(*12*)
Malonic, monohexyl ester	Triethyllead salt	—	(*5, 106*)
Mercaptoacetic	Triethyllead salt	—	(*63*)
o-Mercaptobenzoic	Triethyllead salt	—	(*54*)
2-Naphthalenesulfonic	Triethyllead salt	—	(*62*)
m-Nitrobenzoic (in ethanol)	Triethyllead salt	26	(*55*)
m-Nitrobenzoic (in benzene)	Diethyllead salt	62	(*55*)
p-Nitrobenzoic	Triethyllead salt	25	(*55*)
Nonanoic[a]	Triethyllead salt	—	(*12*)
Octanoic[a]	Triethyllead salt	—	(*12*)
Phenylacetic[a]	Triethyllead salt	—	(*12, 54*)
2-Phenylhydrazinesulfonic[a]	No reaction	—	(*54*)
Propionic[a]	Triethyllead salt	—	(*12, 62*)
3-Quinolinecarboxylic[a]	No reaction	—	(*55*)
Salicylic[a]	Triethyllead salt	—	(*54, 62*)
Stearic[a]	Not identified	—	(*12*)
p-Toluenesulfonic	Triethyllead salt	—	(*53, 62*)
o-Toluenesulfonic	Triethyllead salt	—	(*62*)
Trichloroacetic[a]	Triethyllead salt	—	(*12, 62*)
Valeric[a]	Triethyllead salt	—	(*12*)

[a] In presence of silica gel.

Acid halides react in a manner similar to the halogen acids, although there are differences between the reactivities of individual members. Acetyl chloride with TEL in the presence of silica gel at room temperature gives triethyllead chloride (*12*). Benzoyl chloride likewise reacts; however, only lead chloride could be isolated from the reaction mixture (*12*).

Reaction with Phenols and Thiols

A number of phenols and naphthols have been reacted with TEL in the presence of silica gel to give di- and triethyllead derivatives. Specific compounds which have been prepared in this manner are listed in Table II.

Table II Phenolic Derivatives

Compound	Yield, %	References
Triethyllead phenolate	63.5	(*27, 35*)
Triethyllead picrate	—	(*2*)
Diethylleadbis(*p*-nitrophenolate)	—	(*112*)
Bis(triethyllead) resorcinolate	31.0	(*27, 35*)
Bis(triethyllead) pyrocatecholate	—	(*27*)
Triethyllead *m*-cresolate	—	(*27*)
Triethyllead *p*-cresolate	—	(*27*)
Triethyllead *o*-cresolate	90.0	(*27*)
Triethyllead *o*-bromophenolate	—	(*27*)
Triethyllead 1-naphtholate	—	(*27*)
Triethyllead 2-naphtholate	—	(*27*)
Triethyllead guaiacolate	—	(*27*)

The more acidic phenols—e.g., 2,4-dinitrophenol and picric acid—are also capable of reaction with TEL in the absence of silica gel, although the products obtained have not been identified (*52*).

The thiols react with TEL much more readily than alcohols and most phenols. The presence of silica gel is not required in order to obtain a reaction. Thiols which have been studied are the following: 1-butane-, 1-heptane-, α-toluene-, benzene-, and 2-naphthalenethiol, and mercaptobenzothiazole (*52*). The nature of the products obtained has not yet been published, but they are presumably of the type Et_3PbSR and $Et_2Pb(SR)_2$.

Reaction with Metal and Metalloid Salts

Aluminum chloride in the presence of solvents has been reacted with TEL to form triethyllead chloride and lead chloride (*12, 48, 90*). At the same time, varying amounts of alkylaluminum compounds are formed, depending upon the relative amounts of the reagents (*48*). The reaction of ethylaluminum sesquichloride with TEL likewise results in cleavage of the carbon-lead bond (*48*). The active agent here is probably ethylaluminum dichloride and not diethylaluminum chloride.

A number of metal chlorides have been shown to be reduced by TEL. Thus titanium tetrachloride is converted to a lower oxidation stage, as indicated by the purple color of titanium trichloride (*12*). The reaction products of TEL with titanium tri- and tetrachlorides, the higher chlorides of molybdenum, vanadium, chromium, and manganese, and the halides of the other transition metals of groups IV to VIII, have been proposed as catalysts for the polymerization of olefins (*95*). Thallium trichloride (*57*) and ferric chloride (*48, 89*) are similarly reduced by TEL, with the formation of thallous and ferrous chlorides, while the TEL is converted to a mixture of ethyllead chlorides. Chloroplatinic acid is immediately reduced by TEL to metallic platinum (*48*). Oxidation with stannic chloride has been proposed as a means of removing TEL from dilute solution in gasoline (*25, 43*), since the products—diethyllead and diethyltin dichlorides—are insoluble. No reaction occurs between TEL and the following metal halides: ferrous chloride, ferrous iodide, cobaltous bromide, and nickelous bromide, under the conditions employed for ferric chloride (*48*). However, ferrous chloride in an active form is said to remove TEL from gasoline (*11*).

Phosphorus pentachloride and silicon tetrachloride react with TEL to produce triethyllead chloride (*12*). No mention is made of other products from these reactions.

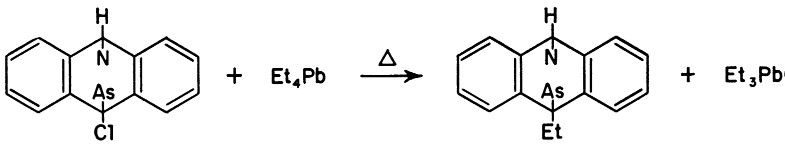
Arsenic trichloride and the analogous phosphorus and antimony compounds have been reacted with TEL to give products indicated by the following equations:

$$Et_4Pb + 3AsCl_3 \xrightarrow[95\text{–}97\%]{100°C.} 3EtAsCl_2 + EtCl + PbCl_2 \ (77)$$

$$Et_4Pb + 3PCl_3 \xrightarrow[89\text{–}96\%]{} 3EtPCl_2 + EtCl + PbCl_2 \ (77)$$

$$Et_4Pb + 3SbCl_3 \xrightarrow[71\%]{} 3EtSbCl_2 + EtCl + PbCl_2 \ (77)$$

The reaction proceeds in stages; at 25°C. only two ethyl groups are cleaved, whereas at 100°C. the reaction proceeds to lead chloride. Refluxing phosphorus trichloride with TEL has also been reported to yield diethylphosphinous chloride (*14*). The reaction of TEL with 10-chloro-5,10-dihydrophenarsazine (Adamsite) is similar to the above reactions (*104*):



The corresponding 10-formyl derivative reacts similarly with TEL to give the 10-ethyl derivative and lead formate (*104*).

Bismuth trichloride also cleaves TEL, though less actively than does aluminum chloride. The products formed are triethyllead chloride, lead chloride, and perhaps ethylbismuth compounds (*48, 91*).

A number of patents and publications deal with the reactions of mercuric salts with TEL. These are the basis for the preparation of certain organic mercury fungicides. In these reactions, indicated below, the lead is converted to an ethyllead or inorganic salt.

$$Et_4Pb + HgCl_2 \xrightarrow[Na_2CO_3]{EtOH} EtHgCl \ (92\%) \ (34, 67, 75, 89)$$

$$Et_4Pb + Na_2SO_4 + HgCl_2 \xrightarrow[Na_2CO_3]{EtOH} (EtHg)_2SO_4 \ (37)$$

$$Et_4Pb + H_3PO_4 + HgO \xrightarrow{EtOH} (EtHg)_nH_{3-n}PO_4 \ (1, 67)$$

(This reaction gives mono, bis, or tris ethylmercuri phosphate depending on ratios of reactants, temperature, and solvent if used.)

$$Et_4Pb + Hg(OAc)_2 \rightarrow EtHgOAc \ (75)$$

Silver and cupric nitrates on reaction with TEL at low temperatures (—70° to —80°C.) yield ethylsilver and ethylcopper plus the triethyllead salt (*56, 116–118*). When the solutions of these metal alkyls are warmed, decomposition of the RM compound occurs with the evolution of butane, ethane, and ethylene. The triethyllead salt is evidently unaffected by this decomposition. The combination of cupric nitrate and TEL in the presence of a monomer such as styrene, methyl methacrylate, or acrylonitrile does not react with formation of ethylcopper. However, the monomers are rapidly polymerized (*6*).

Lead tetraacetate has been reported to react with TEL at 0°C. to give a mixture of triethyllead acetate and lead acetate (*79*).

Triethyllead chloride or bromide is formed from the corresponding diethyllead salt and TEL in solution at room temperature: The reaction is reversible (*4, 82*). This implies a ready interchange of the halogen atom and ethyl radical between different molecules. Such an interchange is most simply shown by observing a mixture of triethyllead chloride and TEL, one of which contains radioactive lead as a tracer (*22*).

Reaction with Metals

There have been a few reported reactions of TEL with active metals. Thus, for example, sodium in liquid ammonia and ethyl ether reacts with TEL to give sodium triethylplumbide and ethane (*50*). The sodium derivative was not isolated, but was reacted with a number of organic halides to give the corresponding unsymmetrical triethyllead compound. The following yields were obtained with these organic halides: n-C_4H_9Br, 91 to 95%; *sec*-C_4H_9Br, 82%; *tert*-C_4H_9Br, nil; $C_6H_5CH_2Cl$, 10%; C_6H_5Br, 77%; and $CH_2{=}CHCH_2Cl$, 72%. Calcium and lithium are also reported to be equally effective for this cleavage (*9*). In contrast, finely divided bismuth does not react with TEL at 100° to 130°C. (*48*).

Redistribution with Other Metal Alkyls

In the presence of a small amount of catalyst such as alkylaluminum or alkyllead halide, Calingaert and coworkers showed that TEL undergoes interchange reactions with other lead alkyls and with certain other metal alkyls to give a mixture of products (*19*, *21*). Where the products have similar types of bonds, as in the R_4Pb mixtures, the amounts of each compound obtained correspond to those expected from a random distribution of the radicals. Compounds which have been reacted with TEL include tetramethyl- and tetra-n-propyllead and a mixture of the two, tetramethyltin, dimethylmercury, and trimethyllead bromide. This reaction has been reviewed (*20*).

Miscellaneous Reactions

It has been reported that TEL reacts with selenious acid to give diethyllead selenite in 15.5% yield (*55*). Phenylarsine has been reacted with TEL at a relatively high temperature (150° to 170°C.), with production of metallic lead (*98*) and arsenobenzene as shown by the equation:

$$Et_4Pb + 2C_6H_5AsH_2 \xrightarrow[\text{Benzene}]{150^\circ \text{ to } 170^\circ\text{C.}} C_6H_5As{=}AsC_6H_5 + Pb + 4C_2H_6$$

The introduction of sulfur dioxide into TEL in a solution of ether containing some water produces diethyllead sulfite in a yield of 99% (*62*). Earlier workers have reported different results from this reaction (*41*, *126*).

The reaction of TEL with carbon tetrachloride takes place slowly at room temperature in ether solution and gives, over a period of 30 days, up to 90% yields of triethyllead chloride plus an unidentified gaseous product. Carbon tetrabromide and hexabromoethane likewise react with TEL in the presence of oxygen to give diethyllead dibromide, with evolution of carbonyl bromide (*65*). A carbon disulfide solution of TEL turns dark red and gives a black precipitate, not identified (*12*).

Very little has been published on so-called Grignard-type reactions with TEL. Chloral has been reported (*93*) to react with TEL at a high temperature, subsequent hydrolysis giving a 20% yield of 1,1,1-trichloro-2-butanol, as indicated by the following equation:

$$CCl_3CHO + Et_4Pb \xrightarrow{170^\circ\text{C.}} Et_3PbOCH(Et)CCl_3 \xrightarrow{HCl} CCl_3CH(Et)OH$$

However, repetition of this reaction by other workers did not confirm these results (*47*). Benzaldehyde and TEL do not react under conditions used for the Grignard reaction (*46*). Likewise ketene, which reacts smoothly with diethylzinc and violently with diethylmagnesium, shows no tendency to react with TEL (*69*).

A number of patents mention or claim the formation of lead derivatives containing olefinic and acetylenic linkages on passing ethylene or acetylene through TEL at ordinary temperatures and pressures (*119*). Other workers have shown, however, that TEL does not react with the active hydrogen of acetylene or ethynylbenzene (*52*).

Reference should be made to the fact that triethylethynyllead and ethynylenebis (triethyllead) have recently been synthesized by a reaction involving triethyllead bromide and sodium acetylide in liquid ammonia (*8*). It is reported that triethylethynyllead is unstable even at −34°C., and disproportionates to ethynylenebis(triethyllead) and acetylene. The bis compound is found to be sensitive to moisture, being immediately destroyed by contact with water.

Finally, TEL, even in dilute solution in gasoline, reacts strongly with an activated clay such as Filtrol (*97*). This is not merely an adsorption, because the lead cannot be removed by any means short of strong acids.

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Uses and Economic Preparation of Organic Arsenic Compounds

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Organoarsenic compounds, generally known as bactericides for strictly medicinal purposes, appear increasingly useful in agricultural as well as in industrial pest control. The similarity in subatomic electronic configurations with nitrogen, phosphorus, and particularly with carbon (greater electropositivity due to greater distance from nucleus) appears to account for the variety of possible molecular structures of the arsenical functional groups, some of which exhibit pesticidal properties. The simplicity and favorable economy of the procedures to prepare known and novel pesticidal compounds may be explained by: the great variety of arsenical functional groups, such as arsonic and arsinic acids, arsine oxides, halides, cycloarsines, etc., and their interchangeability; noninterference with carbon functionalities in the same molecule; and independent substitution on both arsenical and carbon functional groups. Novel compounds were synthesized, including arsenomethane, arsenic-1,2-disulfide, and derivatives, found to be potential agricultural pesticides. The arsonosiloxanes contribute mold-controlling properties to the industrial applications of the regular silicones. Formation of organic nitrogen-base arsenites was investigated and resulted in the determination of the basic constant ($Kb = n \times 10^{-8}$ or greater) as the controlling factor, irrespective of the structure of the organic part.

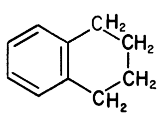
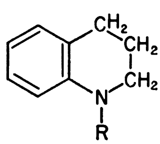
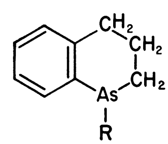
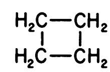
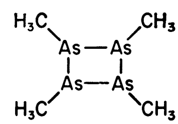
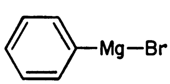
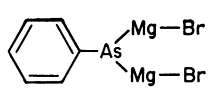
Of all the known organometallics, the thousands of organic arsenicals have retained an impressive lead in number and in variety. The considerable efforts in research and development of these compounds have produced numerous medicinals, a few warfare agents, and some pesticides. It now appears that organic arsenicals have shifted from the predominantly medicinal application as germicides to agricultural uses as pesticides, with more than a substantial promise of carrying their pesticidal properties into the paper pulp, textile, and plastics industries. The improvement of

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materials of established utility by incorporation of the arsenic atom into molecular structures has become a definite possibility.

Arsenic is available as an extremely economical compound commodity in the form of arsenic trioxide, As_2O_3, also called white arsenic. It forms sodium arsenite with caustic soda or sodium hydroxide. This is the starting material for the synthesis of a typical arsenical functional group, the arsono or arsonic acid group. Many organic arsenical structures follow very closely the pattern of nitrogen, phosphorus, and even carbon functionalities. As illustrated in Table I, the similarity of the subatomic

Table I. Functionality of Similar Electronic Structures

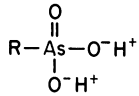
C	N	P	As
s^2 $2s^22p^2$	s^2 $2s^22p^3$	s^2 $2s^22p^6$ $3s^23p^3$	s^2 $2s^22p^6$ $3s^23p^63d^{10}$ $4s^24p^3$
	Outer shells		
— — — —	$R—NH_2$ $R_2═NH$ $R_3≡N$ Amines basic	$R—PH_2$ $R_2═PH$ $R_3≡P$ Phoshines less basic	$R—AsH_2$ $R_2═AsH$ $R_3≡As$ Arsines feebly basic or amphoteric
—	$(H_3C)_3N$ gas, B.P. = 2.9°C.	$(H_3C)_3P$ liquid, B.P. = 40–2°C.	(H_3C) As liquid B.P. = 59–60°C.
—	$R_4≡N^+$ Ammonium very basic	$R_4≡P^+$ Phosphonium very basic	$R_4≡As^+$ Arsonium very basic
 1,2,3,4-Tetrahydro-naphthalene	 1,2,3,4-Tetrahydro-quinoline	Not known	 1,2,3,4-Tetrahydro-arsinoline
 Cyclobutane gas	Unknown	Unknown	 Dimeric polyarsenomethane oil
 Phenylmagnesium bromide Carbon, Grignard	Unknown	Unknown	 Phenylarsine di-(magnesium bromide) Arsenic, Grignard

electronic configuration obviously results in a somewhat similar functionality for carbon, nitrogen, phosphorus, and arsenic. However, the greater electropositivity of arsenic on account of the greater distance of the outer valence shell from the nucleus points to as yet unknown possibilities of organic arsenical structures more closely related to organic carbon than to organic phosphorus or nitrogen.

Another important factor responsible for both the variety and economy of organic arsenical structures is their ability to form functional groups, illustrated in Table II, by syntheses, the simplicity of which is almost unequaled by the reactions of the other elements of similar electronic structures. Thus, the basic synthesis for alkylarsonic acid is Meyer's reaction (*5*). It essentially consists of bringing together

Table II. Synthesis of Typical Arsenical Functional Groups

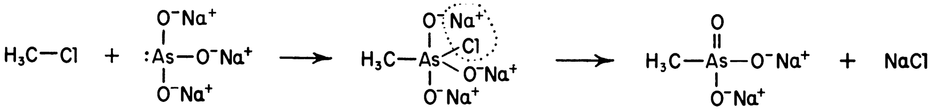
Functional Group



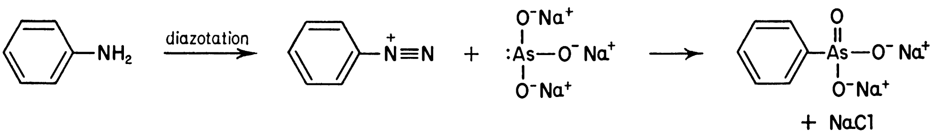
R arsonic acid

Example of Reaction

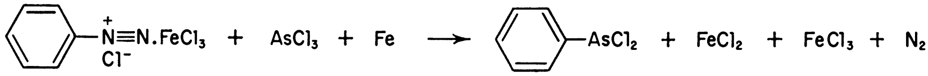
If R is alkyl Meyer's Reaction

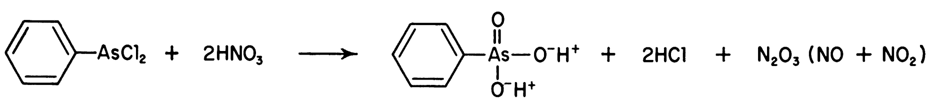


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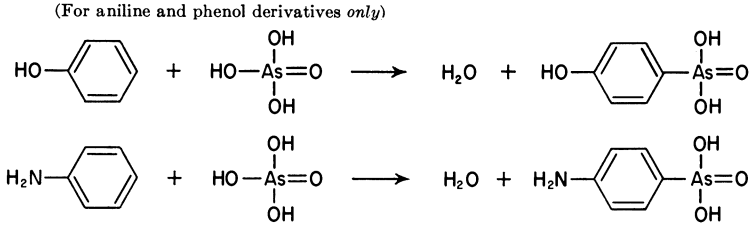


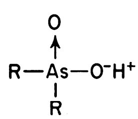
Double Diazonium Salt:





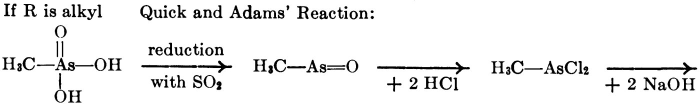
Béchamp's Reaction:
(For aniline and phenol derivatives *only*)

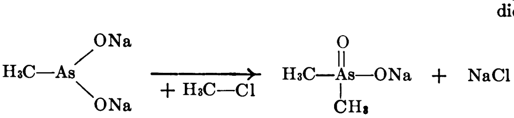




R,R arsinic acid

If R is alkyl Quick and Adams' Reaction:



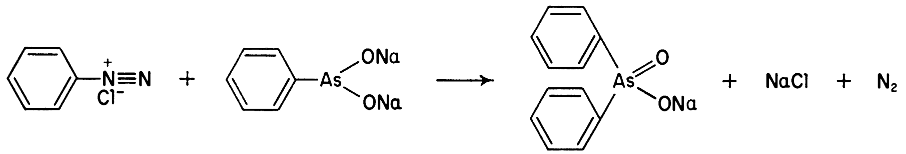


Sodium dimethylarsinate
(sodium cacodylate)

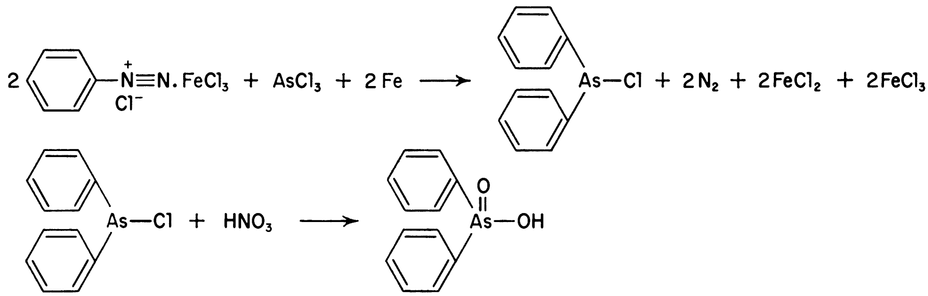
Table II. Synthesis of Typical Arsenical Functional Groups (*continued*)

Example of Reaction

If R is aryl Extended Bart's Reaction:



Double Diazonium Salt:



sodium arsenite in aqueous solution with an aliphatic halide under conditions of pressure, stirring, and a slightly elevated temperature, determined by the liquid or gaseous state of the aliphatic halide. As shown by the equation in Table II, methyl chloride is reacted with sodium arsenite (*6*) at about 60 p.s.i. pressure and at 60°C. to form sodium chloride and disodium methylarsonate. The latter product, an old-time medicinal called Arrhenal (*7*), is now on the market as a new crab grass control agent.

Arylarsonic acids can be synthesized by the classical Bart reaction between a diazonium salt and sodium arsenite, or—if aniline or phenol derivatives are the starting products—by the very economical Béchamp reaction (*2*, *8*). The latter merely consists of fusing together phenols or anilines with *o*-arsenic acid at about 160°C. in an open kettle that permits the dissipation of water formed during the reaction.

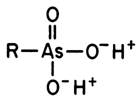
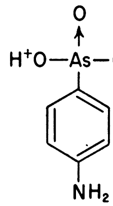
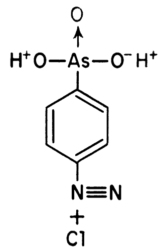
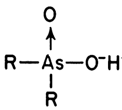
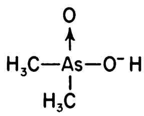
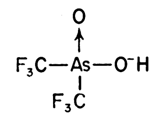
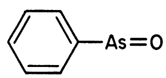
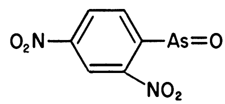
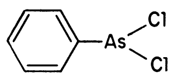
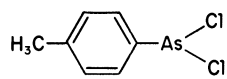
Somewhat related to the Bart reaction is the Russian double diazonium salt decomposition with ferric chloride, arsenic trichloride, and metallic iron (*11*). Although this method is more involved and hence more expensive, it appears more suitable for commercial application, as it is not restricted to certain carbon functional groups like the Béchamp reaction.

Another commercially important arsenical functional group is the arsinic acid, as shown in Table II. The synthesis of this group is equally simple, as it essentially consists of reducing methylarsonic acid to methylarsine oxide and reacting the disodium salt of the latter with an additional mole of methyl halide (*9*). In this manner, dimethylarsinic acid, also called cacodylic acid, is obtained. This compound was found to be a herbicide or agricultural weed killer of considerable efficiency. Research is being carried out now on conversion of this synthesis to large scale production. Aryl derivatives can be made by an extended Bart reaction (*1*) using disodium arylarsenite, or a double diazonium salt, employing 2 moles instead of 1 (for arsonic acids) (*11*).

The great versatility of organoarsenicals with respect to synthesis as well as commercial applications is aptly illustrated by the reaction of cacodylic acid with condensation products of phenols and formaldehyde in which the arsenic is held in an ester-like combination. Alkalies form water-soluble salts of this compound which,

as the free acid, are soluble in the same solvents as the parent phenolic condensation compound (*10*). Evidently, the reaction did not essentially impair either the arsenical or the carbon functionalities. This phenomenon, which seems to hold for all known arsenical functional groups, is further illustrated in Table III. Thus, an arsono

Table III. Substitution on Organic Radical

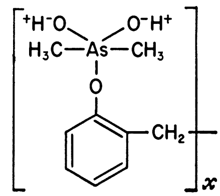
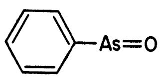
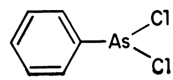
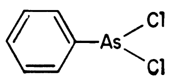
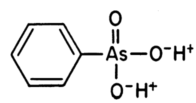
Functional Group	Example	Reaction	Derivative
 R arsonic acid	 *p*-Aminophenylarsonic or arsanilic acid	Diazotation (with HNO_2, HCl)	 *p*-(Diazonium chloride) phenylarsonic acid
 R,R arsinic acid	 Dimethylarsinic or cacodylic acid	Fluorination	 Di-(trifluoromethyl) arsinic acid
R—As=O R arsine oxide	 Phenylarsine oxide	Nitration	 2,4-Dinitrophenylarsine oxide
$R—AsX_2$ R arsine dihalide	 Phenylarsine dichloride	Methylation	 4-Methylphenylarsine dichloride

(arsonic acid) group does not interfere with ordinary diazotation on the aromatic nucleus. Possible also are fluorination, nitration, methylation, and other substitutions on the organic radical. The commercial utilization of this noninterference between organic carbon and arsenic functionalities is found in the possibility of combining the known pesticidal properties of certain organic structures with novel, similar properties of arsenical functional groups.

Still another important factor accountable for the great variety and number of organic arsenical structures is the substitution on the interchangeable arsenical functional groups (arsonic and arsinic acids, arsine oxide, arsine halide), as shown in Table IV. One commercial utilization of substitution on the arsenic is the esterification of cacodylic acid with phenol-formaldehyde resins. Another is the incorporation of arsenic into structures that inherently possess great commercial value, such as the silicones.

In view of all these possibilities of synthesis of organic arsenicals, the development of novel compounds of rather interesting properties was not difficult. This was particularly true with materials that resulted from what appeared to be then a side reaction rather than the intended main synthesis. In this manner compound A-42 was discovered as an unknown impurity with tetramethyltetracycloarsine. As seen in Table V the compound is chemically arsenomethane As-1,2-disulfide (*3*) and exhibits 1,3-tautomerism as well as dimerization. Consequently, metal salts are pos-

Table IV. Substitution on Arsenical Functional Group

Functional Group	Example	Reaction	Derivative
R—As(→O)(—O$^-$H$^+$)—O$^-$H$^+$ R arsonic acid	H_3C—As(→O)—O—H^+, —O—H^+ Methylarsonic acid	*a.* Reduction with SO_2 *b.* Reduction with H_3PO_2	*a.* H_3C—As=O methylarsine oxide *b.* H_3C—As=As—CH_3 Arsenomethane
R—As(→O)(—O$^-$H$^+$)—R R,R arsinic acid	H_3C—As(→O)—O—H^+, —H_3C Dimethylarsinic (cacodylic acid)	Esterification with phenolformaldehyde resins (tautomerism to 3-OH,2 acidic and 1 alcoholic	 (Tentative) arsenical resin
R—As=O R arsine oxide	 Phenylarsine oxide	Chlorination with HCl	 Phenylarsine dichloride
R—As(X)—X R arsine dihalide	 Phenylarsine dichloride	Oxidation with HNO_3	 Phenylarsonic acid

sible by replacement of the active tautomeric hydrogen on the arsenothiol. The methylene group undergoes additive halogenation. The unsubstituted A-42 possesses

Table V. Compound A-42

Tautomerism:

H_3C—As(=S)=As(=S)—CH_3 ←→ H_2C=As(—S$^-$H$^+$)=As(—S$^-$H$^+$)=CH_2

Polymerization:

$2H_3C$—As(=S)=As(=S)—CH_3 ⟶ H_3C—As(=S)—As(=S)—CH_3 / H_3C—As(=S)—As(=S)—CH_3 (As—As bonds linking the two chains)

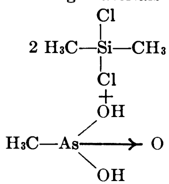
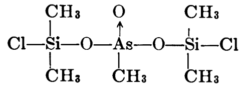
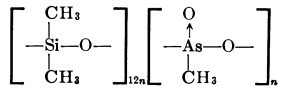
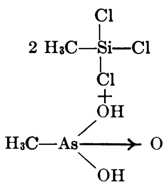
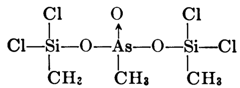
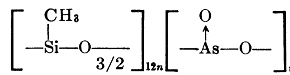
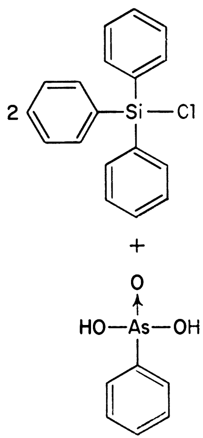
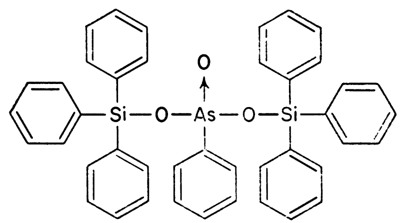
insecticidal properties which are considerably enhanced by chlorination on the methylene group, as shown in Table VI. The disodium salt is a promising defoliant.

Table VI. Structure and Toxicity of Organic Arsenical Pesticides Developed by A. S. & R. Co. Organic Chemistry Laboratory

Code	Compound	Structure	Utility	Pests Controlled
A-42	Arsenomethane	H_3C—As(=S)=As(=S)—CH_3	Insecticide	Rice weevil, southern army worm, not cotton boll weevil
W-84-1	Monochloro-A-42	Cl—H_2C—As(=S)=As(=S)—CH_3	Insecticide	Southern army worm, nematodes, rice weevil, etc.; cotton boll weevil not certain

The arsenic atom can now be incorporated into siloxane structures by a novel reaction between a halosilane and an arsonic acid, as shown in Table VII (4). This

Table VII. Arsenical Silicone Compounds Developed by A. S. & R. Co. Organic Chemistry Laboratory

Compound	Starting Materials		Precursor		Product	Form and Possible Utilities
Methylarsonodimethyl siloxane		→				Transparent, rubbery, for impregnation, rubber additive, blending with other siloxanes.
Methylarsonomethyl siloxane		→				White, powdery, *Does not burn*, rubber additive, flameproofing material, blending with other siloxanes
Bis(triphenylsilyl) phenyl arsonate		→	none	→		White, waxy, for impregnation, wood preservative, paint additive, etc.

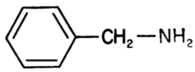
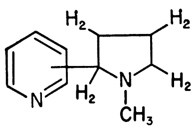
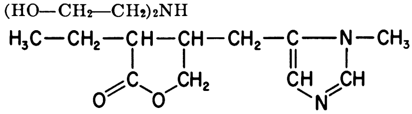
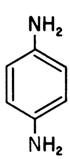
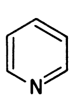
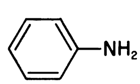
is rather convincing evidence that arsenic not only combines with other organometallic structures, but permits a variety of projected utilities far beyond the classical medicinal or agricultural uses. In the case of the arsonosiloxanes, pest (mold) controlling properties are added to the known water repellency of the conventional silicones.

The Si—O—As bond of the arsonosiloxanes shows that there is still another and, so far, little explored field of arsenicals that are not organometallics or arsenic-carbon bond compounds, but organic nitrogen base arsenites. As a result of experimentation performed to elucidate the critical conditions for arsenite formation, it was found that the organic nitrogen base should not be less basic than is expressed by a K_b (basic constant) of $10^{-8} \times n$ (individual factor). If the K_b is still smaller, no arsenite will be formed. Conversely, if the K_b is greater than $n \times 10^{-8}$, the ease of dissolving arsenic trioxide will be correspondingly greater. Table VIII illustrates this relationship in detail.

The unique properties of organoarsenic, fundamentally evident from the elec-

Table VIII. Organic Nitrogen-Base Arsenites

$(R_3{\equiv}NH)_x^+$ $(H_2AsO_3)_y^-$
R = H, or organic radical, or ring part
$x = 1, y = 2$ for alkanolamines
$x = 1.5, y = 0.5$ for other N bases

Base	Structure	*Kb*	Molar Ratio Base/As_2O_3
Methylamine	$H_3C—NH_2$	4.38×10^{-4}	3/1
Ethylamine	$H_3C—CH_2—NH_2$	5.60×10^{-4}	3/1
Allylamine	$H_2C{=}CH—CH_2—NH_2$	4.9×10^{-5}	3/1
Benzylamine		2.0×10^{-5}	3/1
Monoethanolamine	$HO—CH_2—CH_2—NH_2$	5.3×10^{-6}	0.5/1
Nicotine (alkaloid)	 α,β	1. 7.0×10^{-8} 2. 1.4×11^{-11}	3/1
Diethanolamine	$(HO—CH_2—CH_2)_2NH$	2.7×10^{-7}	0.5/1
Pilocarpine (alkaloid)		1. 7.0×10^{-8} 2. 2.0×10^{-13}	3/1
Triethanolamine	$(HO—CH_2—CH_2)_3N$	5.9×10^{-8}	0.5/1
p-Phenylenediamine		1. 1.10×10^{-8} 2. 3.50×10^{-12}	3/1
Pyridine		1.4×10^{-9}	no arsenite
Aniline		3.83×10^{-10}	no arsenite
Urea	$H_2N—C({=}O)—NH_2$	1.5×10^{-14}	no arsenite

tronic configuration of this transition element, amount to new frontiers for arsenic trioxide, the white arsenic, which has always been readily available as an economical commodity.

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Chemical Corps Experience in the Manufacture of Lewisite

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The U. S. Army Chemical Corps produced 20,000 tons of lewisite [dichloro(2-chlorovinyl)arsine] during World War II. After one false start, an operationally simple batch process was chosen. It involved condensation of acetylene with arsenic trichloride in the presence of mercuric chloride in aqueous hydrochloric acid. Development concurrently was able to devise more economic processes using cheaper catalysts. They were also more complex in equipment and operational requirements. The batch process used less than one year from test tube to tank car. The combined experience demonstrated the usefulness of simplicity in process design when the certainty of early production is the overriding consideration.

Lewisite is the common name for a chemical agent which has dichloro(2-chlorovinyl) arsine as its active constituent. The Chemical Corps manufactured lewisite during World Wars I and II, but it did not receive battlefield test. The agent had not reached the theater of operations in World War I when the Armistice came into effect and in World War II none of the combatants resorted to chemical warfare.

Informed opinion on the value of lewisite as an agent fluctuated, as test results became available. The favorable opinion became strong around 1940 when the decision to manufacture lewisite was made. Large scale tests in 1943 proved that compared to mustard gas, it was not a profitable material to have. Production was stopped, although 20,000 tons had been made.

There was no lack of desire and effort to arrive at a definitive decision earlier, but the properties of lewisite combined with the test facilities available made it practically inevitable that the sequence, as observed, would occur. The Chemical Corps prior to 1940 had neither the laboratory nor field testing facilities needed to reach such a conclusion. As funds became available, existing outside laboratories were diverted to research in chemical warfare and the expansion of local laboratory facilities was expedited. Adequate field test facilities were obtained more slowly. Time was required to form a doctrine for a new type of testing for which funds had previously been extremely limited. Elaborate facilities had to be built. A team containing the diverse skills needed had to be formed, indoctrinated, and trained in an unfamiliar field.

Lewisite is highly toxic, causing profound physiological effects by both inhalation and skin contact. It is stable in most laboratory environments, especially for the short time involved in work with it. On the other hand, it is rapidly hydrolyzed in the presence of moisture which is usually present in earth and vegetation; hence it is largely destroyed over the longer periods involved in field tests.

It was inevitable that when lewisite reached adequate field testing it would fail as an agent, even though laboratory results were very favorable. It was so unstable under average field conditions that much of its toxicity was lost. Unfortunately, laboratory methods at that time had not been developed to a routine which would have predicted such a sequence.

The error in the decision to produce lewisite is, naturally, of historical interest only. It has no bearing on the interesting problems involved in the manufacture and the credit due for their successful solution.

The aluminum chloride process for the manufacture of lewisite was about to be put through the usual pilot plant, production plant routine in early 1941. At that time Conant brought back from England news of a successful reaction of arsenic trichloride and acetylene in the presence of aqueous mercuric chloride. The new method, even from the preliminary evaluation possible, promised substantial operational and equipment simplification. Although the aluminum chloride process had been operated at the pilot plant level, the mercuric chloride process still appeared to be a faster route to production. This proved to be a sound conclusion.

There were other factors involved. Mercuric chloride, while scarce and expensive, was theoretically not consumed and the main drain on stocks would be building up plant inventory. On the other hand, the aluminum chloride charged would all be lost as a useful material constituting, in fact, a substantial disposal problem, contaminated as it would be with arsenic. Depending on a steady supply of aluminum metal for aluminum chloride production did not seem safe, while the war effort demanded the metal for other vital uses.

Unfortunately, engineering was allowed to sell research on the proposition that the only acceptable large scale production process was a continuous one. As a consequence, research abandoned its field of competence and started on the development of process equipment. In a surprisingly short time lewisite was produced and proudly exhibited as the product of a continuous process. The decision was made to start a pilot plant at once.

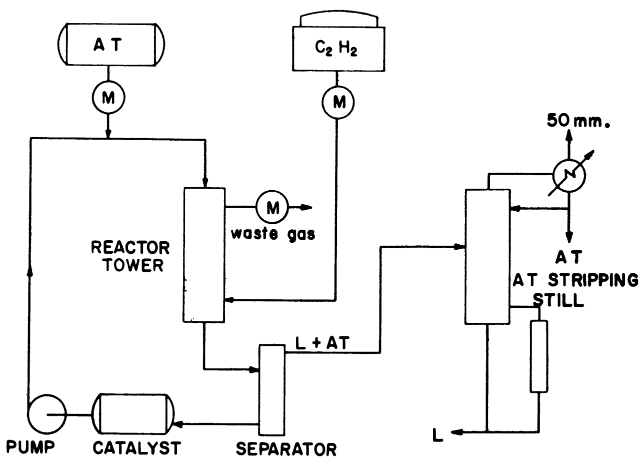


Figure 1. Flow sheet of mercuric chloride continuous process

The pilot plant was unique. Most of the construction was done by engineers and highly skilled and experienced plant operators. Practically no drawings were used. Research men were consultants and described, on the job, the functions of the plant. It was made of whatever could be found available and was a reasonable facsimile of what research said was needed. It was completed in a time extremely short to one familiar with the usual pilot plant schedule. It worked well enough to be evaluated.

On start-up the engineers were dismayed at the tiny stream of lewisite resulting from the large energy input, but it was apparent that research was pleased. Engineering measured streams, calculated ratios, and power consumption. Research, viewing the results, intimated that they were right in line.

A slide rule calculation of the results with introduction of the ultimate production goal was all that was needed to confirm that it was even worse than suspected at first. The final plant would have the largest and/or most reaction towers ever assembled in one spot. In addition, the pumping equipment could have made a substantial contribution in reversing Niagara.

Engineering wrote off the losses; but "continuous" as applied to a lewisite process was an unmentionable word for some time. Batch operation was the order of the day.

The batch operation was successful. The pilot plant operated during most of 1942 and part of 1943. The first production plant was ready in late 1942 and the second and third plants early in 1943. Production was stopped late in 1943, with a total of over 20,000 tons. This was a very substantial achievement, taking into account that the catalyst was first heard of in 1941.

In the meantime, development proceeded along two lines: first, solution of plant production problems and second, consideration of other catalysts and processes. Both efforts were successful.

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Composition of Lewisite

Pure dichloro(2-chlorovinyl)arsine is a colorless, slightly oily, nearly odorless liquid. It has the structure which shows space isomers. Both have been isolated and shown to be stable below 100°C. The often described "geranium" odor of the compound is a consequence of the process of manufacture, being readily identified only in the product of the aluminum chloride process. Vapors of any sample in air are readily detected, but the sensation is usually one of acid irritation rather than of an odor.

Lewisite is a term properly applied to the mass production product containing mainly β-chlorovinyl, mixed with other allied compounds. It is a brownish liquid, inert to steel, and indefinitely stable in closed storage. The materials present are shown in Table I.

Table I. Compositions of Lewisite

Component	B.P., °C.	Composition of Crude: $HgCl_2$ process, %	$AlCl_3$ Process, %	
				After rework
AT, $AsCl_3$	130	40	39	...
*L*1, $ClCH{:}CHAsCl_2$				
cis	150	Nil	Nil	ca. 30
trans	190	55	10.5	ca. 70
*L*2, $(ClCH{:}CH)_2AsCl$	230	5	26.5	
*L*3, $(ClCH{:}CH)_3As$	260	Nil	24	

*L*2 and *L*3 come from further reaction of *L*1 with acetylene. The very high proportion of these materials in the aluminum chloride–controlled condensation, compared to that observed with mercury, is probably due to physical factors. The aluminum chloride reaction is homogeneous and apparently *L*1 is more reactive than *AT*. On the other hand *L*1 is nearly insoluble in aqueous acid and *AT* solubility is

limited. A second, arsenic phase is always present in the mercury process and all the *L*1 is in this phase. Therefore, *AT* having a fair solubility in the catalyst phase has a far higher probability of reacting with any fixed acetylene. *L*1, though more reactive, given the same environment, can react only at the organic-aqueous interface, which reduces the net rate substantially.

The specification composition of lewisite is whatever quality control can maintain in debate with production. Boiling point relations are such as to allow separation of a very pure product. In actual practice, mercury process product was crude more or less completely stripped of *AT*. The aluminum process product did not reach the production stage.

Analysis of lewisite was very accurate and complete. Considering the time involved for development of methods, the accuracy and precision were remarkable. Methods are on file in the Corps for all components of the product and by-product streams. The details can be obtained on application to the Office of the Chief Chemical Officer, Washington 25, D. C.

Processes

The reactions by which lewisite has been made are mentioned in Table II. Methods not using catalysts have been left out.

Table II. List of Processes Studied

Catalyst	Media	Additive	Operation
$AlCl_3$	None	None	Batch—pilot
$HgCl_2$	H_2O	HCl	Batch—prod.
			Cont.—dev.
Cu_2Cl_2	H_2O	$SbCl_3$ + HCl	Batch—res.
		HCl	Batch—dev.
			Cont.—dev.
		Ethanolamine, HCl	Batch—dev.
			Cont.—dev.

Aluminum Chloride Process. The aluminum chloride process was operated in the pilot plant essentially as shown in the flow sheet. The ratio of *AT* to aluminum chloride was 9 to 1. The original scheme was to recover the unreacted *AT* together with product by heating the reaction mass. The result was an explosion near the end of the distillation. The explosion could often be avoided by rigid precautions in the distillation, but it still occurred with sufficient frequency to make the operation unpopular.

It was suspected that an acetylide was present which accumulated to the point where its characteristically rapid decomposition occurred. The remedy proposed was to heat it in driblets to above the decomposition temperature in such a way that the release of energy would not wreck the equipment. A flash boiler heated above the dry point was indicated, but it could not be used on a mixture containing large amounts of relatively nonvolatile aluminum chloride. Hydrochloric acid would extract the aluminum chloride without hydrolyzing the product, if the acid concentration was well over 20%.

The scheme worked. There were no more explosions, either in the laboratory or in the pilot plant.

The disproportionation reactor was the source of the cis isomer. *L*2 and *L*3 in sharing the excess of organic groups with *AT* produce both cis and trans isomers.

The aluminum chloride process makes very good lewisite, but uses an excessive amount of equipment and energy. Also, aluminum chloride is consumed and appears in an unpleasant by-product stream.

Mercuric Chloride Process. The mercuric chloride process uses less equipment, although a little more than was first visualized.

The basic operations in the process involve: the condensation of excess *AT* with

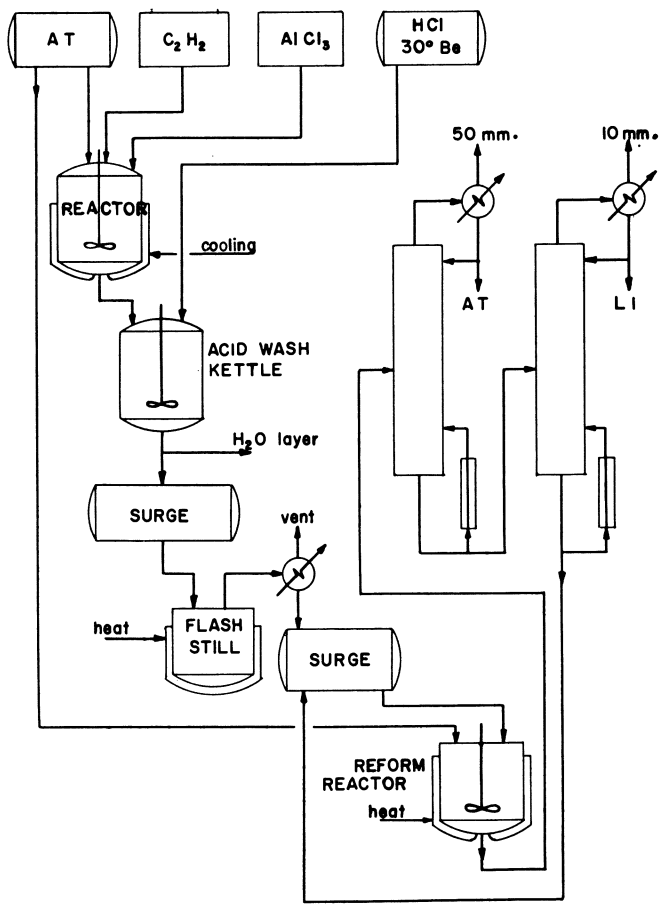


Figure 2. Flow sheet of aluminum chloride process

acetylene, a heating period to react organomercury compounds, separation of the product from the catalyst layer and the vacuum distillation, separation, and recycling of excess *AT*.

This process, while readily workable, has some unfortunate features. The catalyst is heavier than the product and it is expensive. Therefore, it must be dropped and a little of the product dropped with it to wash out lines and valves. In the early stages of development it was found that as *AT* was removed from the mixture, a solid identified as arsenic trioxide separated in copious amounts in the still pot. The process was very dimly regarded until research came up with the idea that 5% of thionyl chloride based on product weight would prevent this, without serious contamination of the product. At the time it saved the process, even if it involved going into the production of thionyl chloride, although later another method was used.

The source of the arsenic trioxide is loss of hydrochloric acid by the system in the formation of the by-product vinyl chloride. As the catalyst is depleted of hydrogen chloride, the concentration drops to the point where a balance is reached between vinyl chloride formation and hydrolysis of *AT*.

$$C_2H_2 + HCl \rightarrow ClCH{:}CH_2$$

$$\tfrac{1}{2}As_2O_3 + 3HCl \rightleftarrows AsOCl + 2HCl + \tfrac{1}{2}H_2O \rightleftarrows AsCl_3 + 1\tfrac{1}{2}H_2O$$

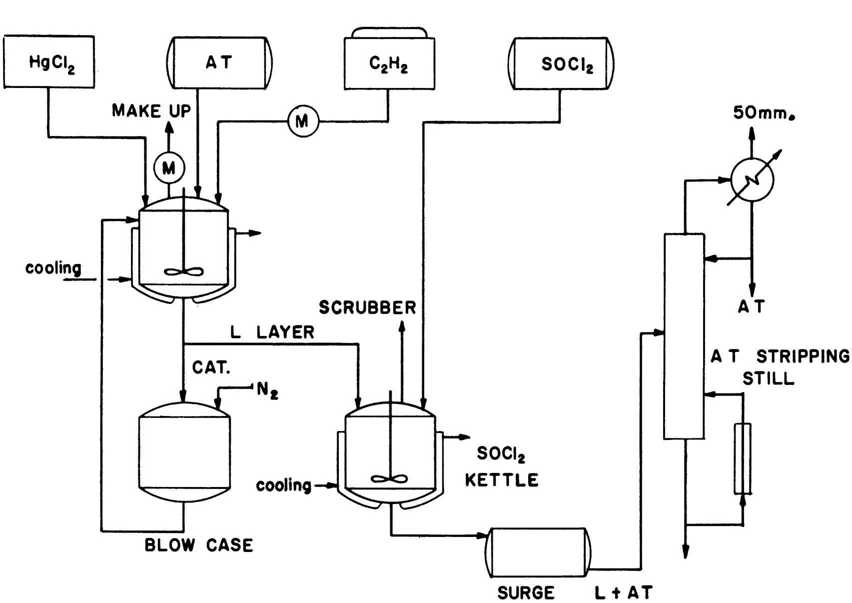


Figure 3. Flow sheet of mercuric chloride batch process

It would be possible to prevent hydrolysis of *AT* by the addition of hydrogen chloride to the reactor, but this would increase acetylene wastage as vinyl chloride. The catalyst on re-use settles down to an acid in water concentration of less than 20%. At this level only a small amount of the acetylene fed is lost as vinyl chloride. As the acid concentration goes above that represented by the constant boiling mixture, the acetylene loss increases more than linearly with concentration.

Plant performance averaged about as shown in Table III.

Table III. Plant Performance

Reactors per plant	32, including 4 extras
Reactor	500-gallon glass-lined
Cycle time	16 hours
Production per cycle	1.5 tons product grade
Distillation	Continuous
Pressure	50 mm. Hg. Temp., 54.5°C.
Reboiler temp.	118°C. Reflux ratio 2 to 1.
Catalyst density	2.25
Product density	1.95

Operationally, the process was satisfactory. Mercury losses were always a worry and the operators occasionally erred in the product catalyst separation.

There was a source of mercury loss which under operating conditions was associated with a loss of acetylene. It was thought, while design was in progress, that the acetylene feed should be dry. This turned out to be unnecessary, as there is a steady loss of water from the catalyst which must be made up periodically. In addition, it was known that arsines, phosphines, etc., would form a sludge in a mercuric chloride solution. Purification was completed by countercurrent tower scrubbing using concentrated sulfuric acid. This was supposed to remove the -ine compounds as well as dry the acetylene. It actually removed several per cent of acetylene and was finally proved to leave part of the impurities.

Mercury losses still occurred in the plant. The cause became apparent as an eventual conclusion from an attempt to duplicate plant losses in development equipment. Extended re-use of catalyst in the laboratory under the most accurate condi-

tions failed to demonstrate any loss. There was considerable discussion of the result, but fortunately the chemist doing the work realized that the engineers running the plant were as accurate with pounds as he was with grams. As this was about the scale ratio involved, he was convinced that there was a loss which he had failed to reproduce. Acetylene was the most probable source of error. He had used cylinder grade, while the plant made it from carbide. It was some time before the analysts were able to identify the impurities as reducing compounds of arsenic, phosphorus, etc. More time was wasted with esoteric methods of purification. Finally an intensive study of Mellor and a closer look at the periodic table led to the conclusion that the material most available, arsenic trichloride, would remove the impurities quantitatively and leave the acetylene untouched. This was quickly and easily demonstrated as true. It was an ideal solution in this case, because vapor from the wash liquid did not have to be removed from the acetylene. Also, *AT* could be used in the existing carbon steel towers installed for the sulfuric acid scrub. Unfortunately, all this was discovered at about the time the orders for closing the plants became enforced.

In the meantime, a characteristic treatment had been tried. It was obvious that the lost mercury was in the lewisite product. There was no other stream leaving the plant. It seemed reasonable to attempt to recover it by product washing and 30% hydrochloric acid solution was the obvious wash liquid. At the same time, the arsenic oxychloride would be converted to *AT*. The first attempts recovered only part of the mercury, although they prevented solid formation during *AT* stripping. It was concluded that the mercury would be in the product in a form other than mercuric chloride. The most obvious change was reduction and chlorine the oxidizer. A small amount of chlorine in the wash solution proved satisfactory and mercury was completely recovered. However, the by-product of this investigation led inevitably to rejection of the method.

The demonstration that mercury was reduced during the reaction led to a search for the reducing agent. It was found in the acetylene feed and the *AT* purification scrub resulted as described.

The introduction of another highly corrosive stream in the plant and the requirement for anhydrous hydrochloric acid were considered too high a price to pay even for avoiding the use of thionyl chloride. If recovery of mercury had been critical, it probably would have been used. As it was, it was economically unsound as long as sufficient thionyl chloride capacity existed and the needed mercury could be procured.

A third improvement, suggested by Dr. Bartlett of Harvard, involved addition of antimony trichloride to the catalyst. It is a powerful promoter for the catalyst and it increases twofold the rate of the condensation reaction. In the catalyst, the concentration could be maintained by incorporating 1% of antimony trichloride in the *AT* feed. It does no harm in the product, but cannot be recovered economically. The impact of the antimony requirement on the war economy was not evaluated, before production of lewisite was stopped.

Cuprous Chloride Catalyst. The cuprous chloride is operated in batch very much as in the mercuric chloride process. It has two important advantages and two serious disadvantages.

Advantages. Cheaper, more available catalyst. Product heavier than the catalyst.

Disadvantages. Much less product, space, time, than for the mercuric chloride catalyst. Larger loss of acetylene as vinyl chloride, based on the lewisite produced.

The process was not discovered until the design on the mercuric chloride system had been decided. The reduction in plant capacity which would have followed a change to the cuprous chloride catalyst was not acceptable as long as mercury could be obtained; as it remained in adequate supply, there was never any serious thought of making the change.

It would have made a very good continuous process, with the exception of the large amount of vinyl chloride produced.

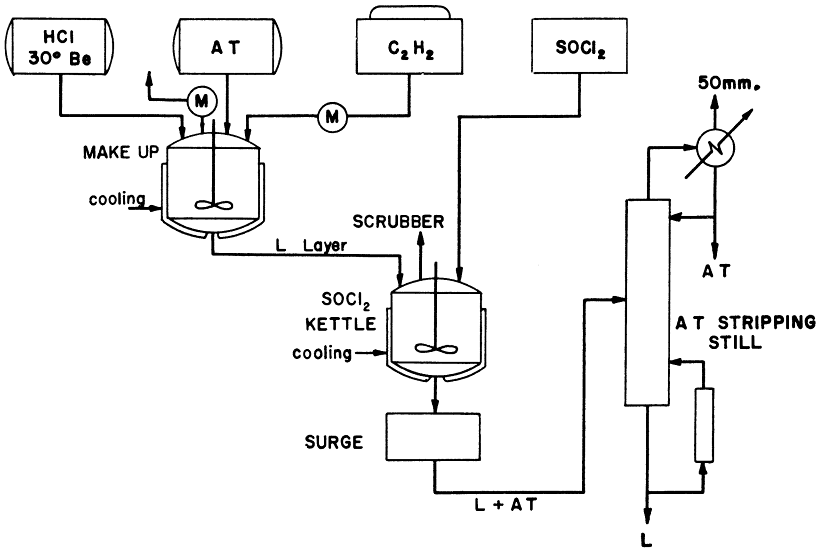


Figure 4. Flow sheet of cuprous chloride batch process

Cuprous Chloride–Ethanolamine Catalyst. The low production rate of the copper catalyst was overcome by the British by using ethanolamine to increase the solubility of the chloride. A very important result was that with ethanolamine the copper chloride–hydrochloric acid is noncorrosive to mild steel. All reactors up to this point had had to be glass lined.

There is usually a disadvantage and in this case it was density relations. *AT* is of higher density than the catalyst. As reaction proceeds, the density of the arsenic layer approaches that of the catalyst and at the end point for specification grade lewisite there is little difference. A solvent is needed to make phase separation possible. Even with this, separation was not good and a continuous separation process was needed. From development work it would have looked something like this:

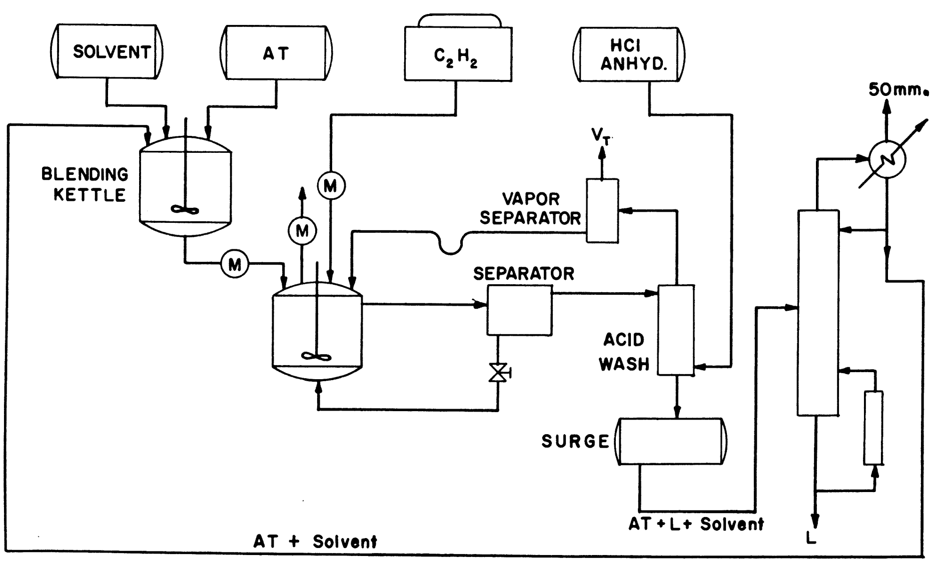


Figure 5. Flow sheet of cuprous chloride–ethanolamine continuous process

A 5-gallon process development setup was operated on this scheme. The separator was nearly 100% efficient in about ¼-gallon size. The remainder of the catalyst was recovered in the hydrochloric acid scrubbing tower, present, primarily to convert arsenic oxychloride to *AT*.

This process could have been used to expand capacity, if there had been occasion to do so. The suitability of mild steel for construction was an overriding advantage.

Other Continuous Processes. All catalysts were, eventually, operated efficiently in continuous systems. In order to be competitive, the mercuric chloride and cuprous chloride catalysts had to be operated in tower systems. The stirred reactor, operated continuously, produces an increased amount of *L*2 and *L*3, the product of condensation of 2 and 3 moles, respectively, of acetylene with 1 of *AT*. This is obvious, when it is considered that all of the condensation of acetylene occurs at the highest level of *L*1 concentration, instead of at an average level of about half of that in the batch reactor. The reaction must be run at a lower total conversion to avoid increase of undesirable polycondensation products. To do this requires a larger stripping still. This was acceptable only with the cuprous chloride–ethanolamine, where the advantages were a sufficient compensation.

A tower system would avoid this by providing an *L*1 concentration gradient along the column about equal to the batch reactor concentration gradient with time. The tower system, previously found low in yield, gave a good space yield when the simple device of filling the column with catalyst solution was adopted. No pumps were needed.

Because of the difference in the catalyst-product density relations, the mercuric chloride and cuprous chloride systems required different arrangements, but the fundamental operation was the same.

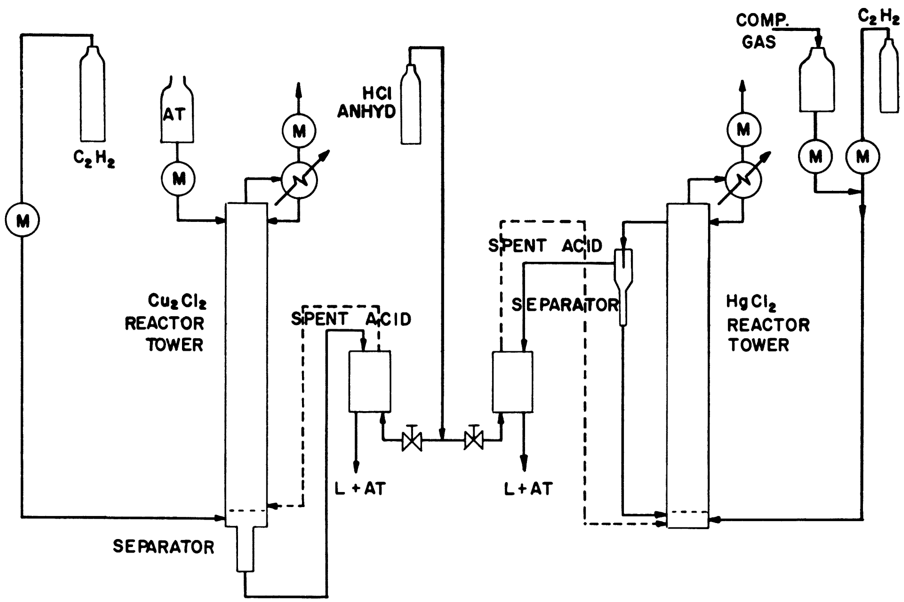


Figure 6. Flow sheet of cuprous chloride and mercuric chloride continuous reactor towers

These towers operated with a minimum of attention. Actually one operator could, and usually did, handle both at once. Separation and level control were self-adjusting to the production rate.

The hydrochloric acid washing, replacing the thionyl chloride treatment, was critical in both processes. In the cuprous chloride system, vinyl chloride production was so high that the thionyl chloride requirement would have been prohibitive. In addition, hydrogen chloride depletion in the lower part of the column (acetylene inlet product separation end) was so great that solids separated. Hydrochloric acid addition was necessary and the overflow from the scrubber was just about balanced by this requirement.

The amount of spent acid overflow was not large, being equal in moles of water content (as a little work with the equations will show) to one half the moles of vinyl chloride produced.

In the mercuric chloride column, where vinyl chloride production is much less, the acid wash is needed for another reason. The mechanism of the reaction producing lewisite involves fixing acetylene as a mercury–vinyl chloride complex which is then transferred to arsenic trichloride. There is a substantial concentration of the organo-mercury intermediate in the absorbing catalyst and it is distributed between the aqueous and the organic phases. In batch operation, a cook period is introduced in the cycle, after the acetylene feed is discontinued, which produces mercuric chloride and lewisite.

The continuous process cannot incorporate this part of the cycle without some fairly demanding arrangements. Fortunately, it was not necessary, as the acid solution broke up the organic complex and extracted the mercury completely. In order to do this, it was necessary to operate the existing acid tower at elevated temperature. It was believed that it would have worked as well at room temperature with a few more transfer units. Development was discontinued before the idea could be tested.

Both tower processes are superior economically to the mercuric chloride batch and both were demonstrated early in the period of plant construction. The mercuric chloride continuous process is superior to the cuprous chloride on the basis of conservation of acetylene and production rate per unit volume. There is no observable mercury loss, with purified acetylene feed, and the over-all production per unit of mercury in plant inventory is higher than in the batch process. While the absorption rate in the tower is less than the average batch rate during the absorption part of the cycle, this is more than made up by continuous operation.

While the economic factors were favorable, the time factor was not. Specially designed, hydrochloric acid–resistant towers, separators, and scrubbers could not be procured on a schedule that would meet the program requirements. In 1942, a few cents per pound was considered as a very small price to pay for speed in production.

It was found possible to make 20,000 tons of lewisite in a little more than 2 years starting from a reaction demonstrated, summarily, in the laboratory. It was done by a slightly lavish use of everything but time, as was demanded by circumstances. The manufacture can be one of the easiest and most economical in the metal-organic field, and it is regretted that no one has ever found any use for the compound. It is a pity to waste such a neat process.

However, if anyone needs a few thousand tons of lewisite, it is not necessary to build a plant. The Chemical Corps still has stock on hand and will be very glad to discuss an arrangement to supply any market up to 4000 tons.

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Chromium Complexes

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Water-soluble, Werner-type chromium complexes of carboxylic acids, which can be used to modify the surface characteristics of many substrates, were developed from the reaction products of chromyl chloride and various organic materials. Typical complexes are Quilon chrome complex (chromium complexes of stearic or myristic acid), used as a water repellent and release agent; Volan (methacrylato chromic chloride), used as a coupling agent in various reinforced plastic laminates; *p*-aminobenzoato chromic chloride, used as an ultraviolet screener; and *p*-nitrobenzoato chromic chloride, used as an antistatic agent. The chemistry of chromium complexes of carboxylic acids, methods of manufacture and application, and various uses are discussed.

Chromium complex commodities are generally acidic solutions of the chromium complex in 2-propanol, water, and sometimes acetone. The complex content will vary between about 20 and 35%, depending on the molecular weight of the carboxylic acid. The amount of water varies from about 5 to 25%, depending upon the complex in question; the acetone content, if any is present, is less than 3%; and usually the remainder of the commodity is 2-propanol.

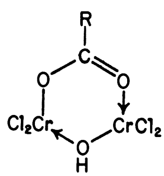
The complexes themselves may be described as reaction products of carboxylic acids and basic chromic chloride:

$$2Cr(OH)Cl_2 + RCOOH \rightarrow Cr_2(OH)Cl_4O_2CR + H_2O \quad (1)$$

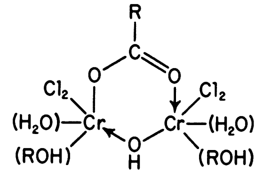
The basic chromic chloride can be prepared in a number of ways, a typical process (*18*) being the reduction of chromyl chloride with an alcohol such as 2-propanol:

$$2CrO_2Cl_2 + 3(CH_3)_2CHOH \rightarrow 2Cr(OH)Cl_2 + 3(CH_3)_2CO + 2H_2O \quad (2)$$

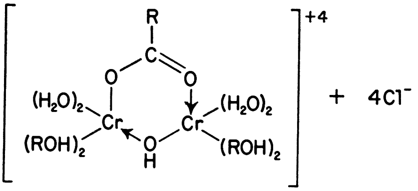
A postulated structure for the monomeric, unhydrated complex is shown by formula I. The complex in the commodity has alcohol and water coordinated with the chromium, and a possible structure for the unpolymerized complex in the commodity is shown by formula II, assuming one water and one alcohol molecule are coordinated with each chromium.



I

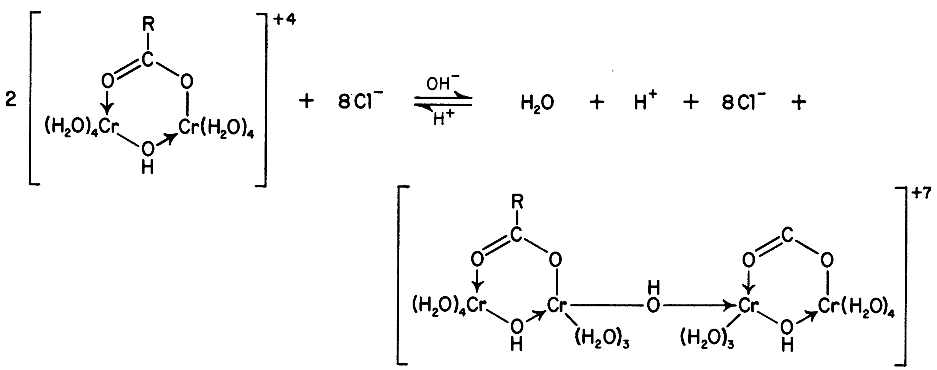

II

In formulas I and II, the chlorine atoms are shown as being coordinated (covalently bound) with the chromium. Probably some exist as chloride ions, even when the commodity contains only a small amount of water. Assuming all the chlorine atoms are ionic and the coordinated chlorine has been replaced with water and alcohol, formula II would be


III

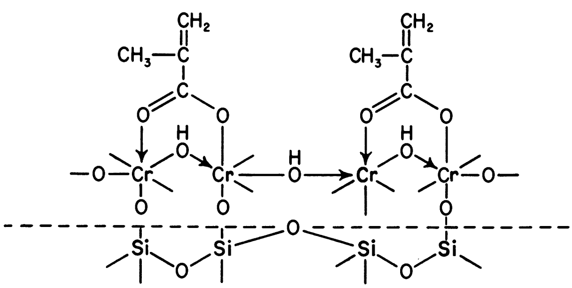
Upon diluting the complex commodity with water, any alcohol groups coordinated with the chromium are replaced with water, and most of the covalently bound chlorine atoms become ionic chloride. The extent of this ionization can be shown by a conductometric titration with silver nitrate. In stearato chromic chloride, immediately after dilution about 74% of the total chloride is ionic, and within several hours 80 to 85% is ionic. In Volan (Du Pont, methacrylato chromic chloride), about 90% of the chloride is ionic upon dilution, and after about 2 hours 95% is ionic. There is also some polymerization of the complex when the commodity is diluted with water, but this is minor compared to the polymerization when the commodity is neutralized or heated.

When the pH of a dilute chromium complex solution is raised from about 3 to 4 to 6, all covalently bound chlorine atoms immediately become ionic and an appreciable amount of polymerization occurs. This polymerization continues as the solution ages as shown by a gradual decrease in pH; the pH of a diluted, unneutralized complex solution changes very little. Probably this decrease in pH is due to the formation of Cr—O(H)—Cr bridges by the elimination of hydrogen ions from the water molecules coordinated to the chromium atoms, resulting in a polymerized complex, rather than to the hydrolysis of chlorine atoms covalently bound to the chromium (*10*). The base used to raise the pH presumably serves to promote the bridging of the chromium atoms through oxygen by shifting the following equilibrium to the right:



The extent of this bridging or polymerization depends on the base used to raise the pH, the amount added, the complex being neutralized, and the degree of dilution. By controlling the polymerization, the complex remains soluble even though of fairly high molecular weight. Heating the complex will also cause polymerization, although probably not as rapidly nor to as great an extent as occurs with increased pH.

When this diluted complex is applied to a substrate and the treated surface is heated, further polymerization occurs to give an insoluble coating which will attach firmly to negatively charged surfaces containing polar groups; the complex is held to the surface by both covalent bonds and polar forces. Surfaces which contain OH, NH_2, COOH, $CONH_2$, SO_3H, and other groups are particularly susceptible to strong bond formation. The bond between Volan and the surface of a glass fiber might be represented as



According to this mechanism, the organo group in the carboxylic acid would be oriented away from the treated surface and, therefore, would give its characteristics to the substrate. The degree of surface coverage by the acid will depend on the amount and the make-up of the complex used. Iler (*12*) calculated that a finely divided amorphous silica, surface area of 100 square meters per gram, treated with approximately an equivalent weight of stearato chromic chloride commodity is essentially completely covered with stearate groups.

Table I. Chromium Complexes[a] and Typical Characteristics They Impart

Acid in Chromium Complex	Characteristics of Treated Surface
Stearic or myristic	Water repellent, nonadhesive
Methacrylic	Reactive toward vinyl polymers
p-Aminobenzoic acid	Opaque to ultraviolet light, reactive toward condensation polymers
2,4-Dihydroxybenzoic	Reactive toward condensation polymers
Sorbic	Reactive toward vinyl polymers
Gluconic	Hydrophilic
p-Nitrobenzoic	Resistant to static build-up
Fluorinated carboxylic acids	Hydrophobic and oleophobic
Cyanoacetic	Reactive toward polymers containing polar groups
Glycine	Reactive toward condensation polymers
Trichloroacetic	Reactive toward polymers containing polar groups, resistant to static build-up
Glycolic	Reactive toward hydroxylated surface
Thioglycolic	Reactive toward sulfur containing polymers or surfaces
Tannic	Reactive toward condensation polymers and hydroxylated vinyl polymers

[a] Complexes and uses are covered by patents (*2, 4, 7–9, 11, 13–16, 19, 20, 22–27*).

Table I gives examples of available chromium complexes and the characteristics they should give to the surface of the treated subtrate. Some potential uses for these or other complexes are insect and mold resistance, oil flotation agents, insolubilization of vinyl-type polymers, treatment of metal surfaces, and chemical intermediates.

Some substances which may be treated readily with chromium complexes are

ceramics, water-insoluble organic and inorganic fillers, vitreous masses, glass, silica, alumina, pigments, clays, wood, paper, cotton, rayon, cellophane, starch, hemp, asbestos, wool, silk, nylon, rayon, other synthetic fibers and fabrics, gelatin, zein, and leather.

Manufacture

The several methods of preparing chromium complex commodities involve the intermediate formation of basic chromic chloride. Methods that either have been or are being used include the following:

Add a solution of chromyl chloride in anhydrous carbon tetrachloride to a solution of the carboxylic acid in anhydrous carbon tetrachloride and anhydrous ethanol, reflux, remove the carbon tetrachloride by distillation, and dilute the product with alcohol and water (*11, 13*).

Add a solution of chromyl chloride in anhydrous carbon tetrachloride to a solution of the alcohol corresponding to the carboxylic acid desired in anhydrous carbon tetrachloride, reflux, remove the carbon tetrachloride by distillation, and dissolve the product in alcohol and water (*13*).

Mix and warm solutions of chromic chloride hexahydrate in glacial acetic acid and the carboxylic acid desired in glacial acetic acid, add acetic anhydride, reflux, evaporate off the acetic acid and acetic anhydride, and take up the product in alcohol and water (*13*).

Prepare basic chromic chloride by reacting chromic chloride hexahydrate with sodium hydroxide in boiling methanol, add a solution of the carboxylic acid in methanol, and reflux (*13*).

Heat at elevated temperature a mixture of chromic chloride hexahydrate and a high melting carboxylic acid, then take up the solid product in alcohol and water (*13*).

React an aqueous solution of chromic oxide in hydrochloric acid, add this solution to an alcohol of less than five carbons, reflux, and then add the carboxylic acid (*17, 18*).

Chromyl chloride for these preparations can be prepared by reacting chromic oxide and hydrochloric acid in a sulfuric acid medium; the chromyl chloride formed can be extracted with carbon tetrachloride. A second method of preparation is to react chromic oxide with hydrochloric acid in an aqueous medium and use this aqueous solution as in the last method given. Anhydrous chromyl chloride can be prepared by reacting a slurry of chromic oxide in sulfuric acid with anhydrous hydrogen chloride. The chromyl chloride separates from the sulfuric acid and can be removed for further reaction (*18*).

Preparation and Application of Treating Solutions

The method used to apply a chromium complex depends upon the complex itself, the surface being treated, and the results desired. All methods involve diluting the complex commodity with water, making any needed pH adjustment, applying the solution to the substrate, drying, in some cases washing the treated substrate, and drying again. In each case, the best method should be determined by experimentation. If the proper method is chosen, the surface modification obtained will be consistent and reproducible. Each step in the application of the complex is described with a brief discussion of the major variables.

Concentration. To obtain an effective treatment, the complex commodity should be diluted with water and not an organic solvent. When an organic system is required, as much water as possible should be added so that the complex can polymerize and bond to the substrate being modified.

The optimum concentration of the treating solution will depend upon the effect desired and the substrate being treated. For materials with a low surface area such as paper, fibers, fabric, cellophane, metals, and masonry, the treating solution should

contain about 0.5 to 5% complex commodity. For small discrete particles, the treating solutions should contain about 2 to 15% complex commodity, depending upon the particle size and surface area of the material. The exact concentration will depend upon the adsorbency of the substrate, treating equipment used, treating time, reactivity of the substrate toward the complex, and wet pickup.

pH Adjustment. The pH of the complex solution should be raised by addition of base. This will increase the efficiency of the treatment, prevent tenderization of materials sensitive to acids, and prevent corrosion of treating equipment. The pH of the complex commodity, as determined by a glass electrode, is about 2; on dilution with water to 2% commodity, the pH is about 3.

The extent and method of pH adjustment depend primarily on the complex and base used. Generally, the pH should be adjusted to an initial value of 4 to 6, providing the complex or treating system and the substrate can tolerate this pH. The pH at which the complexes disassociate or precipitate will vary; complexes of water soluble carboxylic acids generally are more stable at a high pH.

The base should be diluted and added to the complex solution with agitation. The extent of dilution of the base depends upon its strength, but it should be sufficient to prevent local precipitation at the point of addition. A 1% ammonia solution can be added with good agitation to any complex solution, except those of long-chain acids such as myristic or stearic, without precipitation occurring. For a stronger base more dilution is required. If precipitation occurs when first adjusting the pH of a chromium complex, a more dilute neutralizing solution and/or better agitation should be tried. If precipitation still occurs, then a weaker base should be used.

Nitrogenous bases such as ammonia, morpholine, hexamethylenetetramine, piperidine, and melamine are the best compounds for pH adjustment of the chromium complex solution. However, salts of weak acids such as sodium formate, sodium carbonate, and sodium silicate are often used, especially with complexes of highly water-insoluble carboxylic acids. A buffer system has also been used successfully. Quilon (Du Pont) may be partially neutralized with a solution containing 16.5% urea, 5.0% sodium formate, 0.2% formic acid, and 78.3% water; an initial pH of about 4 is obtained. With hexamethylenetetramine or melamine, the pH of an aqueous Quilon solution may be raised to about 5 without precipitation.

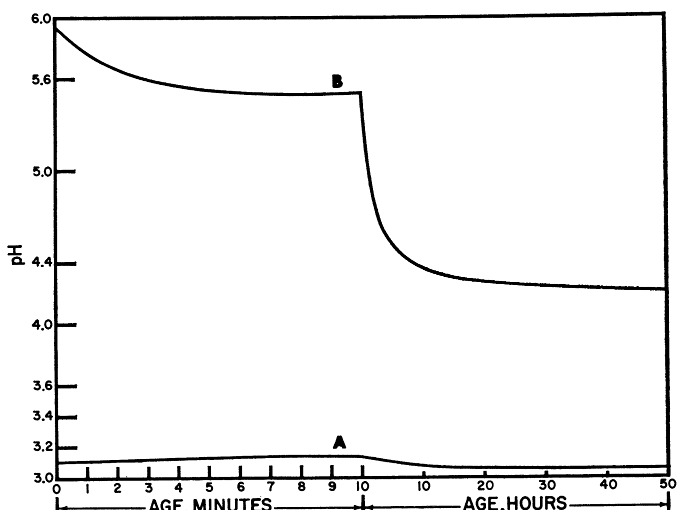


Figure 1. Effect of age on pH of chromium complexes

A. 2% Volan commodity, pH unadjusted

B. 2% Volan commodity, pH adjusted with 1% ammonia

The pH of a freshly prepared complex solution will drop on aging because of polymerization of the chromium. In Figure 1, curve *A* shows the pH decrease of a solution containing 2% Volan commodity, pH unadjusted; curve *B* shows the drop in pH of a 2% Volan solution which has been partially neutralized, 2.2 parts of 1% ammonia per part Volan commodity. This decrease in pH has no effect on the coupling efficiency of the complex, solutions aged 24 hours being equivalent to freshly prepared solutions. Because of this drop in pH, it is preferable to use a given amount of the neutralizing solution per part of complex commodity, instead of adjusting to a given pH. The latter would vary depending upon the age of the solution when the pH was determined, the rate at which the neutralizer was added, and the pH of the dilution water. For Volan, the recommended procedure to adjust the pH is to add 2.2 parts of 1% ammonia per 1 part of commodity.

The effect of using different neutralizers to adjust pH of a complex is shown by a study on Volan (Table II), used commercially to couple laminating resins such as the polyesters to reinforcing materials such as glass fabric. The chromium in the complex bonds to the glass surface, and the methacrylic acid copolymerizes with the resin. To develop the preferred method of applying Volan to glass fabric, a number of neutralizers were evaluated. Glass fabric was treated with 2% Volan neutralized with different amines, dried, washed, and dried again. The treated fabric was made into 12-ply laminates using a polyester resin which were then tested for flexural strength (*6*) after exposure for 3 hours to boiling water. The only variation was the neutralizer used to adjust the pH of the Volan.

Table II. Variation in Coupling Efficiency of Volan with Neutralizer

Neutralizer	pH of Solution	Flexural Strength,[a] P.S.I.
Piperidine	5.7	63,000
Dimethylamine	5.5	58,500
Morpholine	5.5	58,100
Trimethylamine	5.4	56,900
Ammonia	5.3	55,900
Hexamethylenetetramine	5.3	51,600
Pyridine	5.5	49,000
Sodium formate	4.1	48,300

[a] Methods 1031 and 1011.

As shown by the results in Table II, the base has done more than neutralize a portion of the inorganic acid in the complex. The pH of the solution was adjusted to approximately the same value in each case, yet the efficiency of the Volan varies substantially with different bases, piperidine increasing the strength about 30% over pyridine. Ammonia was picked over the other neutralizers for the recommended method of pH adjustment after considering cost, availability, ease of handling, and use efficiency.

The effect of the amount of neutralizer on the use efficiency is shown in Table III. Volan was diluted to 2%, and the pH of the treating solution was adjusted with varying amounts of 1% ammonia. The treated and washed fabric was made into 12-ply polyester laminates and tested for strength (*6*) as in Table II.

Table III. Variation in Coupling Efficiency of Volan with Ammonia Concentration

Pts. 1% NH_3/Pt. Commodity	Treating Soln., pH	Flexural Strength (*6*), P.S.I.
0.0	3.1	52,000
0.3	3.7	52,100
1.1	5.0	56,400
2.2	5.6	60,700
3.5	6.0	57,900

After a certain level, increasing the amount of neutralizer decreases the efficiency of the complex, even though precipitation has not occurred. This should be considered when determining the optimum amount of neutralizer to use. The data in Table III are applicable only to the ammonia-Volan system and cannot necessarily be applied to any other neutralizer-complex combination.

During the treatment of alkaline surfaces, such as with fillers, pH adjustment of the complex solution is not required unless the treating equipment or the substrate will not tolerate a low pH.

Application Techniques. The treating solutions can be applied to continuous surfaces in such ways as dipping, brushing, and spraying, depending on the physical and chemical properties of the substrate, the equipment available, and the result desired. With paper, the chromium complex can be applied at the size press, calender stack, or water boxes, by spraying, transfer rolls, or immersion, the preferred point being at the size press. For continuous surfaces such as metals or shaped articles, the treating solution is best applied by dipping or spraying. Discontinuous surfaces such as fillers or pigments can be treated by stirring the particles in the complex solution and removing excess solution by filtering. When used to modify a treating system such as a poly(vinyl acetate) emulsion or a starch size, the complex commodity can be added directly to the system after pH adjustment. With all substrates, the treatment should be uniform, and excess complex should be removed.

With most substrates, a simple laboratory procedure to obtain treated material for evaluation is to dip or stir the substrate in treating solutions of various concentrations, remove excess solution by squeeze rolls or filtration, and oven dry.

Drying. The treated substrate can be dried in several ways, such as by oven, heat lamp, or drum dryer. The drying temperature should be from about 100° to 150°C., depending on the substrate. Cellulosic products, synthetic fabrics, and other materials that cannot stand high temperatures are dried at 100° to 120°C. Glass fabric, inorganic particles, and like materials are normally dried at 130° to 150°C. Drying should continue only until all surface moisture is removed, as prolonged heating may be detrimental. The heating step is necessary, because it further polymerizes the complex and bonds it to the surface of the substrate. The maximum temperatures chromium complexes can withstand are not known. With Volan-treated glass fabric, two drying cycles of 15 minutes at 190°C. after treating and washing have a detrimental effect on the coupling efficiency, but one cycle at 150°C. after treatment and one at 190°C. after washing have little effect on the efficiency of the complex.

If it is necessary to dry the treated surface at room temperature, a reasonably effective treatment is to use a complex treating solution prepared at 100°C. or else boiled after preparation. This method is inferior to the use of elevated drying temperatures.

Washing of Treated Substrate. Washing of a treated and dried substrate normally increases the effectiveness of the complex. The washing serves to remove both salts formed during pH adjustment and excess complex. Substrates treated with complexes that are hydrophobing agents are not washed. The washing and subsequent drying are best carried out by the same procedure used to apply the complex, making certain the treated material is thoroughly wet by the water. Except for some alkaline

Table IV. Chromium Retention on Washing Volan-Treated Glass Fabric

% Volan in Soln.	Neutralizer	Washes	% Chromium on Fabric
1.0	Sodium formate	0	0.019
		1	0.009
1.25	Ammonia	0	0.024
		1	0.024
1.50	Ammonia	0	0.035
		1	0.033
		2	0.032

substrates, the treated material must be heat dried before washing; otherwise most of the complex will be removed. If the complex has been properly applied, washing will only remove excess complex. Table IV gives data on the washing of glass fabric treated with Volan, using ammonia and sodium formate as neutralizers, and drying at 150°C.

When sodium formate is used to adjust the pH, half of the chromium is removed. This is probably one reason sodium formate is inferior to ammonia as a neutralizer (Table II).

Uses for Chromium Complexes

Chromium complexes can be used to modify the surface characteristics of many substrates: The characteristics imparted will be determined by the carboxylic acid in the complex. Thus, the chromium complex of myristic or stearic acid will render a surface hydrophobic and resistant to adhesive forces, whereas the chromium complex of methacrylic acid will render a surface reactive toward various adhesives or polymers, especially vinyl-type polymers.

Some typical uses of chromium complexes are discussed. A number of these applications have been evaluated in the laboratory only, and before being applicable on a commercial scale, further developmental work would be desirable. Treatment with chromium complexes can impart a green coloration to the substrate because of the color of the complex commodity. This coloration varies with the amount of complex applied, but at normal treating levels it is noticeable only with white or very light colored substrates.

Chromium Complexes on Paper. Chromium complexes impart properties such as water repellency, sizing, grease resistance, and adhesive release to various paper surface as shown by Tables V to X. The paper was treated with the chromium com-

Table V. Water Repellency on Chromium Complex–Treated Papers

	Roll-Off[a] on Various Papers at % Commodity Concn.				
Acid in Complex	Water leaf 0.25	0.3% rosin kraft 0.13	0.6% rosin kraft 0.10	Gumming kraft 0.08	Liner board 0.40
Stearic	80	100	100	90	90
Palmitic	30	100	100	100	80
Myristic	80	100	100	90	90

[a] Roll-off ratings.

Rating	Behavior of Water Drop on Paper at 45° Angle
0	Short continuous trail, wider than drop, stopping in less than an inch.
30	Short broken trail, stopping in 2 to 4 inches.
50	½ of trail wetted.
70	4 to 8 spherical drops per inch, starting about 3 inches from point of application and scattered over remainder of trail.
80	Same as 70, except 2 to 4 spherical drops.
90	Same as 70, except less than 2 spherical drops.
100	Rolls off perfectly or leaves only 1 or 2 drops over a 10-inch trail.

Table VI. Water Repellency of 0.6% Rosin Sized Kraft as Function of Complex Concentration

	Roll-Off[a] at % Commodity				
Acid in Complex	1.0	0.25	0.1	0.05	0.03
Stearic	100	100	100	90	90
Palmitic	100	100	100	100	90
Myristic	100	100	100	90	90

[a] See footnote *a*, Table V.

Table VII. Grease Resistance of 60-Pound Vegetable Parchment Treated with Chromium Complexes

Acid in Complex	Spot Areas[a] at % Commodity Concn.						
	1.0	0.25	0.1	0.08	0.05	0.03	Control
Stearic	1.9	1.1	1.4	2.7	3.5	3.7	6.7
Palmitic	1.1	4.0	4.9	3.3	3.1	4.3	6.7
Myristic	0.2	2.4	3.1	3.3	2.2	2.7	6.7

[a] Square inches of spot produced in 24 hours by 5 drops of turpentine colored with turkey red oil on 4 × 4 inch sheet.

Table VIII. Scotch Cellophane Tape Release from 60-Pound Vegetable Parchment

Acid in Complex	% Releasing Force[a] Required at % Commodity Concn.					
	1.0	0.25	0.1	0.08	0.05	0.03
Stearic	45	42	46	44	44	64
Palmitic	46	54	45	37	40	35
Myristic	43	55	57	56	58	67

[a] % of force to release control of Scotch tape, 1 inch wide and pulled at 20 linear inches per minute:

$$\% = \frac{\text{lb./linear inch for sample}}{\text{lb./linear inch for control}} \times 100$$

Table IX. Sizing Effect of Stearato Chromic Chloride on 25-Pound Kraft, Rosin Sized

Lb. Commodity/10,000 Sq. Ft. Paper	Ink Penetration,[a] Min.
0.0	0.25
0.04	1.5
0.08	2.0
0.17	3.0
0.29	5.5
0.42	15.0
0.73	30.0

[a] Small boats, formed by folding up ¼ inch on the four sides of 2-inch square of treated paper, were floated on a common permanent blue-black ink: Time for 3 ink spots to become visible on upper surface of paper.

Table X. Sizing Effect of Stearato Chromic Chloride on 50-Pound Kraft, 1.25% Rosin

Lb. Commodity/10,000 Sq. Ft. Paper	Absorption[a], G./100 Sq. Cm./5 Min.		
	Wire side	Felt side	Av.
0.0	0.485	0.417	0.451
0.12	0.357	0.335	0.346
0.18	0.342	0.329	0.336
0.30	0.321	0.312	0.316
0.48	0.315	0.282	0.299

[a] Cobb size test, weight per unit area increase after exposing paper to 25°C. tap water for 5 minutes (*28*).

plex at the concentration indicated after adjusting the pH to 3 to 4 with a urea–sodium formate–formic acid neutralizing solution containing 16.5, 5.0, and 0.2%, respectively.

Stearato Chromic Chloride–Wet Strength Resins for Paper Sizing. Stearato chromic chloride tub sizing of kraft hand sheets, beater-treated with a high level of wet strength resins, increases the wet strength of the paper above that obtainable with the resin alone. Table XI presents the data obtained with untreated and Quilon-treated hand sheets made with several urea–formaldehyde and melamine–formaldehyde resins. Quilon tub sizing of the hand sheets prepared with wet strength resins appreciably increases the wet tensile strength and gives a substantial reduction in Cobb size value (increased sizing).

Table XI. Effect of Quilon Tub Sizing on Hand Sheets[a] Made with Wet Strength Resins

	No Quilon		Quilon Treated	
Resin Type[b]	Cobb size, g./sq. m.[c]	Wet tensile strength[d]	Cobb size, g./sq. m.[c]	Wet tensile strength[d]
Cationic UF	24.0	24.8	15.6	46.9
	21.2	28.7	14.3	52.8
	21.6	36.0	15.8	56.9
	21.8	27.0	16.0	56.5
	22.5	22.5	17.4	36.8
Cationic MF	20.9	42.5	16.5	53.2
Anionic UF	23.8	15.8	17.0	39.4
	23.7	19.7	18.0	42.5
No resin	22.8	6.5	19.8	8.7

[a] Prepared from unbleached spruce kraft pulp of 780 Schopper-Riegler freeness, with 1.2% rosin size, 1.8% alum, and 3% resin solids; basis weight of sheets = 50 lb. (24 × 36–500); cured at 120°C. for 30 minutes; Quilon retention, 1.5% commodity; Quilon applied at pH 4.5.

[b] UF, urea–formaldehyde resin; MF, melamine–formaldehyde resin.

[c] Exposure to water, 2 minutes at 25°C. (*28*).

[d] Tensile strength determined on ½ × 6 inch tensile strips, from each major direction of paper by Thwing-Albert Electro-Hydraulic tensile tester (Thwing-Albert Instrument Co., Philadelphia, Pa.). Wet tensile determined after 24-hour soak in distilled water as % of dry control.

Poly(vinyl Resin)–Chromium Complex Combinations. Chromium complexes are effective insolubilizers for poly(vinyl resins) such as poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA). In particular, combinations of Quilon and Volan with Du Pont's Elvacet poly(vinyl acetate) emulsion (such as 81–900) and Du Pont's Elvanol poly(vinyl alcohol) (such as 72–60 or 72–51) have been investigated. These combinations impart such properties as improved rub and wet bond resistance, increased resistance to blushing and blocking, higher sealing temperatures, and increased grease resistance to paper products. The complex commodity can be added directly to the vinyl resins and neutralization is required only where light weight papers are to be coated.

The addition of Quilon to poly(vinyl acetate) causes thickening which increases on aging, but this can be controlled by immediate use or by the use of a viscosity stabilizer such as Emulphor ON (polyethylene ethers of fatty alcohols, General Dyestuffs Corp.), as shown in Table XII.

Table XII. Effect of Viscosity of Chromium Complex Addition to Poly(vinyl Resins)

	Viscosity in Centipoises at 25°C. after				
Resin-Complex Combination	Initial	1 day	2 weeks	1 month	3 months
1. Poly(vinyl acetate) (Elvacet 81–900)	820	820	820	820	820
2. PVAc + 5% Quilon	3,550	9,800	50,000	—	—
3. PVAc + 5% Quilon + 5% Emulphor ON	1,820	—	6,300	—	6,700
4. PVAc + 5% Volan	820	870	2,030	2,570	—
5. 50% PVAc + 50% PVA (Elvano 72–51, 9%)	1,240	1,300	1,430	1,500	—
6. Combn. 5 + 5% Quilon	2,200	6,200	24,500	50,000	—
7. 50% PVAc + 50% starch (6%)	88	86		Continued thin	
8. Combn. 7 + 5% Quilon	115	390	900	4,000	—

The addition of chromium complexes to poly(vinyl acetate) adhesives increases their water resistance (Table XIII). The complexes were added to Elvacet 81–900 at a 5% chromium concentration and allowed to age for varying periods. The adhesive was applied to kraft liner boards with a drawbar or a brush, laminates were prepared, and the wet bond strength of the adhesives was evaluated before heat cure. Volan-modified poly(vinyl acetate) needs to be aged to give good wet strength. Heat curing at 200°F. for 2 minutes will improve the wet strength of the complex–poly(vinyl acetate) adhesives, but not of poly(vinyl acetate) alone. The use of Emul-

Table XIII. Bond Strength of Chromium Complex–Poly(vinyl Acetate) Adhesives

	Bond Strength after 24-Hr. Soak			
		Sample Age, Days[a]		
Sample	Initial	10	21	32
Elvacet 81–900	Very poor	—	—	—
+ stearato chromic chloride	Good	—	Good	Good
+ Volan (methacrylato chromic chloride)	Poor	Fair	Fair—good	Good
+ propionato chromic chloride	Poor	Poor	Poor	Poor—fair

[a] Age of sample stored as liquids, not age of bonded laminates which were tested after overnight aging.

phor ON with the stearato chromic chloride–poly(vinyl acetate) to decrease the viscosity (Table XII) does not affect the wet bond strength.

The use of Quilon in a poly(vinyl acetate) system will increase the grease and wet rub resistance as shown by the data in Table XIV. Two types of fiberboard

Table XIV. Greaseproof Coating on Groundwood Board

Board	Coating[a] Retention, Lb./100 Sq. Ft.	Grease Resistance, Sec.[b]
All groundwood	None	20
	2.8–3.9	1800+
	1.4	1800+
Groundwood, patent coat	None	390
	2.8–4.6	1800+

[a] Coating composition: 100 parts by weight Elvacet 81–900, 3.5 parts Santicizer B-16 (Monsanto Chemical Co., butyl phthalyl butyl glycolate), 7 parts titanium dioxide, 5 parts Quilon, and 18 parts water. The ingredients were mixed in the order given and agitated for 5 to 10 minutes.

[b] (*29*), the turpentine was applied to the laboratory-coated side of board.

were treated on one side with a Quilon–poly(vinyl acetate)–titanium dioxide composition. The boards were an all-groundwood board and a groundwood board which had one side coated with patent, the composition being applied to the nonpatent side. Also, a combination of Elvacet 81–900 (74.1%) and Quilon (7.4%) in water (18.5%) will give excellent grease resistance to kraft paper when applied by a two-strike application to obtain a final coating weight of 15 pounds per ream. In addition, the sheets do not block when moistened and subjected to a pressure of 300 p.s.i. for 2 days.

A study of various surface coatings for asbestos-cement shingles to prevent efflorescence or whitening (bloom) indicated that Quilon gave good water repellency, but did not prevent efflorescence. A combination treatment of 10% solids poly(vinyl alcohol) or poly(vinyl acetate) insolubilized with 20 to 40 parts of Quilon based on vinyl solids results in excellent water holdout and stops efflorescence. This treatment is equal to or better than the commercial plastic coatings studied in water repellency, liquid holdout, as a water vapor barrier, and in resistance to efflorescence. The data from this study are given in Table XV. Elvanol 72–60 and Elvacet 81–900 were modified with varying amounts of Quilon, without pH adjustment. The treating preparations were brush coated onto uncoated shingles, 11 grams per square foot. These were oven dried for 5 to 10 minutes at 110°C., cooled, and tested.

Chromium Complexes on Textiles. Chromium complexes of long-chained carboxylic acids are of value as both a primary and a supplementary water-repellent treatment for textiles. Materials such as cotton and wool and synthetic fabrics such as nylon and felt are rendered water repellent. The treatment, depending on the material and method of application, is often resistant to both laundering and dry cleaning.

Table XV. Treatment of Asbestos-Cement Shingles for Water Repellency and Antibloom

Vinyl Type	Vinyl % solids	Parts Quilon Commodity/Pt. Vinyl Solids	Effect on Appearance	Water Roll-Off at 45° Angle	Bloom Test[a] [b]
PVA	10	0	None	Fair—wets	Moderate
		5	None	Good—wets	Slight
		10	Slight green	Good—sl. wet	Slight
		20	Slight green	Good	Slight
PVAc	10	0	None	Fair—wets	Severe
		10	None	Fair—wets	Moderate
		20	Slight green	F—good—wets	Slight
		30	Slight green	F—good—wets	Sl.—none[c]
		40	Mod. green	Good	None
PVAc	27	0	None	Good	Severe[c]
		15	Slight green	Very good	Severe[c]
		60	Green	VG—excellent	None[d]

[a] Impermeability of coating: Coated surface of a 4-inch square of shingle is inscribed with paraffin wax; enclosed area is filled with 40 cc. of distilled water which is allowed to evaporate to dryness at room temperature (usually 24 hours); when dry, the test area should be the same color as the control area; if bloom (whitening, efflorescence) is observed, it is reported as slight, moderate or severe.
[b] Water penetrated through the panel in 1 hour and dried in 16 hours.
[c] Very slow penetration, wet after 18 hours, and dry in 24 hours.
[d] Almost no penetration and required 48 hours to dry.

A comparison of various neutralizers with Quilon for treating cotton is given in Table XVI. The cotton was dipped in a 1% Quilon solution at the pH shown, wrung to 100% wet retention, and cured by two passes on a drum dryer (whose surface temperature at equilibrium averaged 120°C.).

Table XVI. Effect of Neutralizer on Quilon-Treated Cotton Fabric[a]

Neutralizer	Soln. pH	Before Laundering[b]: Spray rating[d]	Before Laundering[b]: % immersion absorption[e]	Spray Rating after Laundering[c]
Urea–sodium formate–formic acid buffer	2.8	70+	20.5	25
	3.5	80−	22.5	25+
	4.0	80−	25.7	50
Ammonia[f]	3.5	70+	19.1	0
	4.3	80−	19.8	25
	5.0	80	20.8	50
Diethanolamine[g]	3.5	80−	18.8	25
	4.3	80	21.1	25+
	5.0	80+	22.4	50
Hexamethylenetetramine[g]	3.5	80−	20.6	60
	4.3	80+	20.9	60
	5.0	80++	22.3	60

[a] White broadcloth, averaging 17.3 grams per sq. ft.
[b] The untreated cloth before laundering had a 0 spray rating and an immersion absorption value of 74%.
[c] Laundering done by standard cycle (–) in Launder-ometer (Atlas Electric Devices Co., Chicago, Ill.) (5), Section IV.
[d] After being sprayed and shaken of excess surface water, the samples were rated as follows (5):

100	No sticking or wetting of upper surface.
90	Slight sticking or wetting of upper surface.
80	Wetting of upper surface at spray points.
70	Partial wetting of whole upper surface.
50	Complete wetting of whole upper surface.
0	Complete wetting of whole upper and lower surfaces.

[e] The water picked up was determined (5) after submerging the test samples below the surface for 20 minutes, removing excess moisture, and weighing.
[f] 0.5% solution; local precipitation obtained on addition.
[g] 1% solution; local precipitation obtained on addition of the diethanolamine.

The buffered neutralizing solution and hexamethylenetetramine are superior to ammonia and diethanolamine in this use of Quilon.

The effect of increasing amounts of hexamethylenetetramine (HMTA) to adjust the pH of a Quilon treating solution for cotton broadcloth is shown in Table XVII. The hexamethylenetetramine was added to the diluted Quilon as a 10% aqueous solution. The treated fabric was wrung to a 100% pickup and dried on the drum dryer. All of the treating solutions were stable for at least 16 hours.

Table XVII. Increasing Amounts of Neutralizer and Quilon Efficiency[a]

% Quilon Soln.	Ml. 10% HMTA/400 G. Soln.	Soln. pH	Before Laundering: Spray rating	Before Laundering: % immersion absorption	After 1 Laundering: Spray rating	After 1 Laundering: % immersion absorption
0	0	6.0	0	74	0	74
1	10	2.7	80++	22.3	60	—
1	20.8	5.2	80++	23.8	50	28.1
1	27.0	5.3	80+	25.7	50	27.3
1	60.0	5.7	80	29.5	50	29.5
2	59.0	5.4	80+	29.6	50	25.9
3	85.0	5.5	90−	32.1	50	24.6
5	30.1	4.6	100−	26.5	50	22.4

[a] For details of tests see footnotes *a*, *b*, *c*, *d*, and *e*, Table XVI.

In the pH range from 5 to 5.5 for a 1% Quilon treating solution, there is essentially no loss in water resistance, as measured by immersion absorption tests, after the standard laundering cycle. The water repellency, as measured by spray rating, was decreased.

The tenderization effect of Quilon solutions, pH adjusted with different neutralizers, is shown in Table XVIII. The Quilon was applied to samples by tub sizing as

Table XVIII. Neutralizer and Tenderization of Quilon-Treated 8-Ounce White Cotton Duck

Neutralizer[a]: Type	Neutralizer[a]: % of 2% commodity[b]	Soln. pH	Tensile Strength, % of Untreated Control: Fresh Soln.	Fresh Soln.: Accelerated test[c]	Aged Soln.[d]	Aged Soln.[d]: Accelerated test[c]
None	—	2.6	67	20	61	18
Urea-formate	110	4.3	87	105	86	105
Melamine	11	4.3	58	27	76	22
Sodium silicate	5	4.3	68	26	85	25
Dicyandiamide	25	2.7	64	58	72	60
	50	2.7	66	72	68	68
Urea-formate–dicyandiamide	110–25	4.3	95	107	84	100
Melamine–dicyandiamide	11–25	4.3	85	68	87	73
Sodium silicate–dicyandiamide	5–25	4.3	78	81	82	76

[a] Melamine and dicyandiamide added as solids; sodium silicate added as 5% aqueous solution; urea-formate added as aqueous solution: 16.5% urea, 5.0% sodium formate, 0.2% formic acid, and 78.3% water.
[b] % solids of neutralizer added.
[c] Samples heated at 130°C. for 6.5 hours; untreated control retained 84% of initial tensile strength.
[d] 4 hours of aging before fabric treatment.

a 2% solution at the pH shown. These were wrung to 100% pickup, drum-dried, and tested for tensile strength in the warp direction on a Thwing-Albert Electro-Hydraulic tensile tester. The retention of strength is based on the strength of the untreated substrate:

$$\frac{\text{Tensile strength of treated substrate}}{\text{Tensile strength of untreated substrate}} \times 100$$

In all cases, the treated fabric had excellent water resistance. The Quilon solution with urea-formate neutralizer is best from a tenderization effect but has the least stability (about 4 hours). The urea-formate–dicyandiamide mixture gives solutions that are stable for 3 days and is almost equivalent on tenderization. In similar tests with both acetate and viscose rayon cloth, there was little if any tenderization of the fabric, regardless of the neutralizer.

The use of Quilon as a water repellent for various types of wool weaves, both before and after dry cleaning, is shown in Table XIX. The fabric was treated on a commercial scale with about 1% Quilon to a 70% pickup, wrung, and dried. The pH of the treating solution was adjusted to 3 to 4 before application. The results show that dry cleaning has little effect on the dynamic absorption of Quilon treated wool.

Table XIX. Effect of Dry Cleaning on Quilon-Treated Wool

Wool Sample	Treatment	Dynamic Absorption, % Water Pickup[a] Before cleaning	After cleaning[b]
Black	None	84	98
	Quilon	38	38
Gray	None	67	62
	Quilon	33	37
Striped	None	64	78
	Quilon	33	38
Blue and white	None	105	119
	Quilon	47	55
Check	None	78	68
	Quilon	36	38

[a] Fabric samples, 3 × 3 inches, were cut on bias, placed in water-filled pint jars containing twenty ¼-inch steel balls, and tumbled 20 minutes on Launder-ometer at 80°F. Results are averages of 3 samples (5).
[b] 7 × 7 inch samples were placed in pint jars containing 200 ml. of Stoddard solvent and tumbled 20 minutes on Launder-ometer at 80°F. Three cleaning cycles were employed, allowing the samples to air dry and condition overnight between cycles.

Similar results were obtained with Quilon-treated wool felt at retentions of 1 to 3%. The immersion absorption was from 50 to 80% less for the Quilon treated, as compared to untreated controls.

Several chromium complexes were evaluated on wool gabardine, before and after dry cleaning. The data are shown in Table XX. The pH of the complexes was adjusted to 3 to 4 before application.

Table XX. Chromium Complexes on Wool Gabardine

Acid in Complex	Spray Rating[a] at Commodity Concn. Before Cleaning 1.0	1.3	After 3 Cleanings 1.0	1.3	Dynamic Absorption[b] % of Dry Weight Pickup at Commodity Concn. Before Cleaning 1.0	1.3	After 3 Cleanings[c] 1.0	1.3
Stearic	80+	90	80	80+	34	33	38	39
Palmitic	70+	—	80−	—	31	—	40	—
Myristic	—	90−	—	80	—	32	—	38
Control	70+	70+	70	70	50	50	53	53

[a] Spray rating, footnote *d*, Table XVI.
[b] Dynamic absorption, footnote *a*, Table XIX.
[c] Dry cleaning, footnote *b*, Table XIX.

To show that different types of material can be treated with Quilon to impart water resistance, several synthetic fabrics were treated on commercial equipment, the

Table XXI. Water Resistance of Quilon-Treated Synthetic Fabrics

Fabric	% Quilon Retained on Fabric	Before Dry Cleaning: Spray rating[b]	% dynamic absorption[c]	After Dry Cleaning[a]: Spray rating[b]	% dynamic absorption[c]
Dacron staple[d]	None	0	107	0	62
	2	80	51	70	37
Dacron filament	None	0	13	0	15
	2	70	9	50	11
Orlon filament[e]	None	0	27	0	42
	2	90	23	50+	30
Wool–Orlon	0	0	119	0	139
	0.5	80+	21	80	40
	1.3	90	21	80	30
	2	80+	22	70+	42

[a] Dry cleaning, footnote *b*, Table XIX.
[b] Spray rating, footnote *d*, Table XVI.
[c] Dynamic absorption, footnote *a*, Table XIX.
[d] Du Pont, polyester fiber.
[e] Du Pont, acrylic fiber.

pH of the Quilon treating solution being adjusted to 3 to 4 before application. The water resistance before and after dry cleaning is shown in Table XXI. The results are comparable between treated and untreated for a given fabric but are not necessarily comparable between different fabrics.

All four fabrics have been rendered water resistant by the Quilon, the treatment of the blend of wool and Orlon acrylic fiber showing particularly good resistance to removal by dry cleaning. Nylon raincoat fabric has been treated with 2% Quilon using a detergent (0.05% Igepal CA, General Aniline and Film Corp.) prewash and afterwash. The prewashed fabric, after dip treatment, being wrung to 60% pickup, and oven dried at 105°C. had a spray rating of 80 after treatment and 90 following the detergent afterwash.

Quilon is an excellent water repellent treatment for felt hat bodies. Depending on the hat body and Quilon retention, spray ratings of 80 to 100%, immersion absorptions of 15 to 20%, and water penetration times through the crown of over 90 hours can be obtained. Table XXII gives typical results obtained with two different felt hats treated with unneutralized Quilon on a commercial scale.

Table XXII. Water Resistance of Felt Hats Treated with Quilon

Hat Felt	Treatment	Hr. for Crown Penetration by 100 Ml. H_2O	% Immersion Absorption[a]
A	1,3, and 5 min. soak in 1% Quilon	>90	22–20
	1,3, and 5 min. soak in 2% Quilon	>90	21–22
	1,3, and 5 min. soak in 3% Quilon	>90	21–22
	None	<10	95
B	1 to 3% Quilon (rough body)	>90	20
	1 to 3% Quilon (finished body)	>90	22–25
	None (rough body)	<15	100

[a] Immersion absorption, footnote *e*, Table XVI.

Antistatic Properties of Chromium Complexes. Chromium complexes such as those of *p*-nitrophenylacetic acid, *p*-nitrobenzoic acid, phenylacetic acid, trichloroacetic acid, and thioglycollic acid have shown utility as antistatic agents (*20*). Table XXIII gives the results obtained in laboratory experiments with the chromium complexes of *p*-nitrophenylacetic acid (PNP) and *p*-nitrobenzoic acid (PNB) on nylon and Dacron (Du Pont polyester fiber). The complexes were applied by dipping the fabric in the diluted solutions, wringing, and oven drying at 190°F. for 5 minutes.

Table XXIII. Antistatic Properties Imparted by Chromium Complexes

Material	Acid in Complex	% Complex in Soln.	Diluent	Complex Commodity Retention, Mg./Sq. Ft.	Static Discharge, Volts[a]
Nylon			Control		760
	PNP	0.3	2-Propanol	2	260
		0.6	Water	4	130
		0.9	2-Propanol	6	76
	PNB	0.6	Ethanol	4	300
	PNP	1.2	Water	8	88
Dacron					960
	PNP	0.36	Water	4	140
	PNB	0.36	Water	4	590
	PNP	1.2	Water	8	100

[a] Measured at 78°F. and 72% RH by methods of Lehmicke (*21*) and Chandler (*3*). Fabric charged by rubbing it 10 times with a neoprene-gloved hand and dropping it into an aluminum beaker, insulated from the ground and connected to a voltmeter. The voltage generated is measured by the voltmeter.

Use of Chromium Complexes to Screen Ultraviolet Radiations. A number of chromium complexes show a high ultraviolet absorptive capacity over a wide range of the ultraviolet spectrum. Clear films such as cellophane treated with these complexes effectively screen ultraviolet radiation. A single layer of cellophane treated with the complex of *p*-aminobenzoic acid will eliminate 90% of the ultraviolet radia-

tions in the 2400- to 3400-A. range incident to the treated sheet. Materials that are degraded by these radiations such as paint films, fabrics, dyes, and light-sensitive polymers could be protected by applying a surface treatment of a suitable complex or by wrapping in a treated film.

The acids themselves screen ultraviolet radiations, but they are not substantive to the materials being treated as are chromium complexes. By combining the acid with basic chromic chloride, the maximum absorption peak may be shifted significantly, often to the more desirable higher ranges. The complexes in Table XXIV had good absorptive capacities with peak efficiencies at the wave lengths shown.

Table XXIV. Complexes with Good Absorptive Capacities

Acid in Complex	Peak, A.
p-Aminobenzoic acid	3000 to 3350
p-Methoxycinnamic acid	3150
5-(Phenylazo)salicylic acid	3800
4-(Nitrothiophene)carboxylic acid	3200

A 1% solution of the chromium complex of *p*-aminobenzoic acid, neutralized to pH 4.5 to 5.5 with dilute ammonia, imparts an ultraviolet protective coating to cellophane. This coating is permanent to dry cleaning with Perclene (3 cycles in Launderometer), is stable on continuous exposure to ultraviolet radiations, and has a moderate resistance to mild soap washes.

Flame Retardant–Water Repellent Treatments. A flame retardant–water repellent composition for treatment of flammable materials has been developed (*1*). The composition consists of ammonium sulfamate, a chromium complex such as stearato or myristato chromic chloride, dicyandiamide, and boric acid.

Pieces of 50-pound basis weight (24 × 36–500) kraft paper were treated with a composition containing 10 parts by weight of ammonium sulfamate, 0.12 part of Quilon based on chromium content, 1 part of dicyandiamide, 1 part of boric acid, and 86 parts of water. The pieces were dipped in the treating solution, wrung, and drum dried at 105°C. The papers were then aged in an oven at 200°F. for 23 hours. The properties of the treated paper are given in Table XXV.

Table XXV. Paper Treated for Flame Retardance and Water Repellency

Test	Before Aging	After Aging
Flame test		
Afterglow, sec.	0	0
Char length, inches	3.0	2.6
Tensile strength, lb. per inch of width		
Machine direction	24.8	26.8
Cross direction	18.6	17.4
pH of paper	3.6	3.7
Water repellency	Excellent	Excellent

Use of Chromium Complexes as Coupling Agents. As mentioned previously, Volan is used commercially as a coupling agent for reinforced plastic laminates, the chromium of the complex bonding to the reinforcing material and the organic acid presumably reacting with the laminating resin.

A comparison on glass fabric reinforced polyester resin laminates of Volan, Quilon, and no coupling agent is given in Table XXVI. The 181-style glass fabric was treated with 2% complex solutions neutralized with ammonia, dried at 150°C., washed, and dried again. Test laminates (12-ply) were prepared from the fabric using a polyester resin.

Table XXVI. Comparison of Coupling Agents for Reinforced Plastic Agents

Coupling Agent	Flexural Strength, × 10^3 P.S.I.[a] Dry	After 3 hr. in boiling water
None	50.0	28.0–30.0
Quilon	27.8	26.3
Volan	65.0	52.2

[a] (*6*), Methods 1031 and 1011.

As would be expected, the Quilon acts as a parting agent and not a coupling agent.

Table XXVII gives more detailed strength characteristics of 12-ply laminates made

Table XXVII. Polyester Laminates Reinforced with Volan-A Finished Glass Fabric

Polyester Resin Used	Flexural Strength, × 10^3 P.S.I.		Flexural Modulus of Elasticity, × 10^6 P.S.I.		Tensile Strength, × 10^3 P.S.I.		Compressive Strength, × 10^3 P.S.I.	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
USAF spec.[b]	50.0	45.0	2.70	2.50	40.0	38.0	35.0	30.0
A	68.0	57.8	3.57	2.98	48.2	47.8	48.5	37.5
B	74.2	60.1	3.52	3.40	51.5	51.5	—	—

[a] (*6*), Methods 1031 and 1011; wet strength determined after exposure in boiling water for 2 hours.
[b] (*30*).

from glass fabric with the preferred Volan treatment [Volan A finish: 2% commodity, pH adjusted with 2.2 parts 1% ammonia, the treated dried fabric being washed (*4*)] and two polyester resins.

Use of Chromium Complexes to Treat Fillers. Fillers are often used to extend polymer systems. Many fillers, inorganic or organic, may be treated with chromium complexes to modify their surface characteristics. A calcium carbonate filler treated with Quilon is much more water repellent and more easily dispersed in organic systems than the corresponding untreated filler. Experiments were carried out using Volan-treated calcium carbonate to see if the treatment improved their efficiency in reinforced plastic laminates. The calcium carbonate (surface area, 25 sq. meters per gram) was treated with dilute, ammonia-neutralized Volan solutions, filtered, washed with water, and dried. The treated filler and a washed, untreated control were stirred in a polyester resin (20% filler on weight of resin). It took over four times as long to stir in the untreated filler as the Volan treated. The filled resin was then used to prepare laminates from Volan-A finished glass fabric. The results of strength measurements of the laminates are shown in Table XXVIII. The flexural strength was determined (*6*), the wet flexural strength being determined after exposure for 2 hours in boiling water.

Table XXVIII. Volan-Treated Calcium Carbonate Fillers in Glass Fabric Reinforced Plastic Laminates

Treatment Filler	% Ignition Loss	Flexural Strength, × 10^3 P.S.I. Dry	Wet
No filler added to resin control	38	64.5	56.4
Washed $CaCO_3$, no Volan	39	45.6	39.6
$CaCO_3$ treated with 0.5% Volan	34	59.6	53.7
$CaCO_3$ treated with 0.2% Volan	36	60.1	53.8

Both the wet and dry flexural strengths of the laminates containing the Volan-treated calcium carbonate were substantially higher than in the laminate containing the

untreated filler. These results were duplicated substantially with other Volan-treated fillers, using chopped strand and needled glass fiber mats as the reinforcing medium.

Use of Chromium Complexes on Leather and Other Materials. SIDE LEATHER. Quilon is employed as a posttannage agent on side leather to impart properties not obtained in the normal tannage. Improved properties obtained in the finished leather are water, chemical, and perspiration resistance and permanent lubrication. Because of these properties, the finished leather articles such as safety and dress shoes, golf bags, and work gloves generally have an improved life and better appearance during wear. The Quilon may be applied in the drum, before or after the fat liquoring operation. The chromium complex is applied to chrome tanned, vegetable tanned, or chrome tanned–vegetable retanned stock, the effect being more pronounced with the latter two processes.

SUEDE GARMENT LEATHER. Chromium complexes of acids such as myristic and stearic impart water repellence and dry cleanability, act as a permanent lubricant on sheepskin suede garment leather. The complex acts as a replacement for all or part of the fat liquors which otherwise would be extracted by the dry cleaning solvent, leaving the suede in a stiff, unlubricated state. Because of the water repellency, the complex treated suede has excellent resistance to water-borne stains. The complex is applied to the suede after tannage and before or after fat liquoring, if fat liquors are used in addition to the complex.

MISCELLANEOUS. Table XXIX gives some commercial and laboratory tested uses of chromium complexes.

Table XXIX. Miscellaneous Uses of Chromium Complexes

Some Commercial Uses for Quilon and Properties

Treatment of ice cube bags	Release and repellency
Greaseproof and parchment paper for packaging	
Frozen food	Release
Synthetic and natural rubber	Release
Treated paper board as boxes for flowers, fish, wet vegetables	Water repellency
Treated paper plates	Water and grease resistance
Treated boxes for baked goods	Release
Miscellaneous treated paper	
Building paper	Repellency
Paper to protect wet concrete	
Casualty blankets	
Paper rugs	
Treated felt hats	Repellency
Treated textiles, especially felts for automobiles	Repellency
Decorative fiber glass fabrics	Repellency and bonds resin to fabric for soft hand
Treated cellophane pressure-sensitive tape	Release

Laboratory Evaluated Uses for Quilon

Agent to prevent chocolate stainthrough in candy boxes

Treatment on asphalt tiles prevents blocking when the tiles are stacked

Addition to poly(vinyl alcohol) imparted grease and water resistance to paper plates; coating did not block at 350°F.

Imparts water repellency to filter paper used as an adsorbent medium in gas purification equipment

Imparts water repellency to laminating paper impregnated with rubber latex–glycerine for use in paper–aluminum foil laminates

Reduces moisture wicking when glass fiber cordage is wetted

Treatment of dyed paper substantially reduces dye bleed

Imparts water repellency to jute, kraft, vulcanized, and chipboard

Imparts anticrocking properties to nylon frieze if applied as a boiling treatment

Treatment of glass fiber window screening improves spray repellency

Treatment with poly(vinyl alcohol) imparts water repellency and desired stiffness to nylon shoe mesh

Addition to lacquer-thinner compositions for straw hat treatment gives significant improvement in maintaining wet stiffness

Water absorptiveness reduced over 50% by treatment of vulcanized fiber

Hat bands have 100 rating roll-off when treated to 1% retention

Retards oil migration on asbestos tape

Effective masonry sealer (prevents water penetration) on bricks, cement blocks, mortar, and cinder blocks

Effective in starch sizes to increase the lactic acid resistance of paperboard and to improve the anchorage of the wax coatings used as finish

Aqueous DDT emulsion containing a wetting agent, although mothproofing wool serge, decreases the water repellency of the wool. Addition of Quilon to the emulsion gives treated wool a water repellency equal to untreated control and decreased water absorption characteristics

Improves wet burst strength of solid fiberboard

Use as Coupling Agents

Chromium complexes of amino and hydroxy acids are of interest as coupling agents for reinforced epoxy and phenolic resin laminates

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Molybdenum Chelates, Esters, and Organometallics

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Molybdenum, a transition element, displays multiple valence states and a great complexing tendency. Molybdenum chelates, esters, and organometallics are the important industrial compounds. Chelates are formed with nitrogen, sulfur, and oxygen linkages. Esters are derivatives of molybdic acid with alcohols, phenols, or hydroxy acids. The organometallic compounds comprise alkyl and aryl derivatives as well as complexes with carbonyls, cyanides, olefins, and acetylenes. The preparation and physical properties of some of these compounds are indicated.

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Molybdenum has shared in the renascence of interest in metals chemistry which was sparked by uranium at the start of World War II. Molybdenum's other congeners of subgroups VI of the Periodic Chart, chromium and tungsten, have similarly proved to be heavy metals with an unusual chemistry. Although over 90% of the molybdenum produced is consumed in metallurgical applications of increasing importance, an industrial chemical technology is also taking shape with the expanding use of molybdenum in catalysts, colors, and lubricants.

Molybdenum, with valence states of 0, 2, 3, 4, 5, and 6, is a transition element capable of forming many stable compounds. It also has enormous complexing power, especially in the higher valences. The combination of several valence possibilities and unusual complexing capacity leads to a great variety of possible organic and inorganic derivatives.

The chemistry of molybdenum, whether it is in the field of inorganics or organics, is exceedingly complicated. The complications have been compounded by inaccuracies in data and the related interpretations to be found in the early literature. The vast progress in structural chemistry is, however, rapidly pointing the way for general understanding and agreement.

In spite of the complications of molybdenum chemistry, at least one large class of molybdenum organics—the chelates—is familiar to the industrial chemist. Molybdenum compounds of this type are widely used for the preparation of brilliant organic pigments, an application which consumes about 450,000 pounds of molybdenum a year. Molybdenum chelates are treated first in this paper, because of their firm position in industrial chemistry.

Molybdenum esters have been extensively discussed, particularly in the older literature. Although they do not at present receive any known commercial applications, they are discussed as the second important class of organomolybdenum.

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Molybdenum compounds which belong to the organometallic class, at least in the broader sense of this term, have been intensively studied in recent years. Although molybdenum, like many of the other transition metals, does not readily form true alkyl and aryl derivatives, it does form a series of compounds which can best be described as substituted carbonyls. Because of their great interest in fundamental chemistry and their potentialities for industrial utilization, this group of compounds is discussed at some length in the final section of this paper.

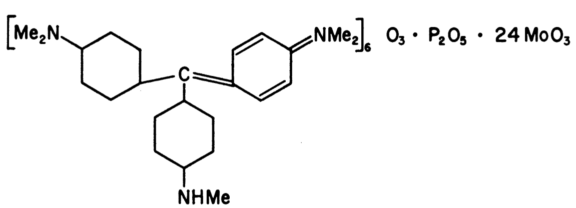
One reason for the increased tempo of research and development work on molybdenum chemicals is that a wider variety of molybdenum compounds suitable as research reagents has been prepared. Molybdenumcarbonyl, the pentachloride and other halides, and a variety of soluble isopoly and heteropoly salts have recently been added to the sulfide, oxide, and simple molybdates as materials available for research purposes.

Molybdenum Chelates

Molybdenum chelate compounds consist of complexes with Mo—N—C, Mo—S—C, and Mo—O—C linkages. Most of the known compounds are complex molybdate anions probably formed by chelate coordination with polybasic acids and polyhydroxy compounds like oxalic acid, phthalic acid, salicylic acid, and catechol. Of the many chelate compounds which have been satisfactorily characterized with distinctive properties, those involving Mo—N—C bonding have evoked the greatest commercial interest thus far.

Molybdenum-Nitrogen-Carbon System. Perhaps the best known of these Mo—N—C complexes are those used in the manufacture of organic pigments for the printing ink industry. Basic dyestuffs such as methyl violet, Victoria pure blue, Brilliant Green, Rhodamine 6G, and Thioflavine T are precipitated by phosphomolybdic acid to give the PMA colors, and by phosphotungstomolybdic acid to give the PMTA colors (*40*).

A good example of a phosphomolybdate toner or color lake is shown by the suggested chemical formula for the complex with methyl violet:



These organic pigments are characterized by brilliance, strength, and resistance to light, heat, and water.

The structure of the PMA colors is very similar to that of the starting dyestuffs, most of which exist as salts, usually chlorides or sulfates. The formation of a PMA color is simply the replacement, in solution, of a lightweight anion by a much heavier one, thus causing precipitation. The phosphomolybdate anion can replace a halide anion in one of the dyestuffs; approximately six or seven molecules of dye are required for each molecule of phosphomolybdic acid used (*40*).

PMA colors are manufactured by a three-step process: solution of the dyestuff in water at controlled pH and temperature; preparation of the complex acid solution from soluble phosphate and molybdate salts with the addition of mineral acid to bring the pH within the range of 3 to 4 at a temperature of 20° to 30°C.; and addition of the complex acid solution to the dyestuff solution at a controlled rate and with controlled agitation. The precipitated pigment is then stabilized by heating, followed by a final treatment with excess of the complex acid (*40*).

Production of PMA and PMTA colors as organic pigments represents the most important single use for molybdenum compounds. Annual world consumption of

molybdenum in this application totals 450,000 pounds, with the printing ink industry accounting for a predominant portion of this market. Other areas where these brilliant colors find application are in the tinting and shading of white paper to offset the yellowness of natural paper stock, in the manufacture of colored paper, and in water colors and enamels for children's toys.

Other vivid colors might be produced from heteropoly acids and various basic organic dyes. Among likely starting materials for new organic pigments are silicomolybdic acids with a molybdenum-silicon atomic ratio of 12 to 1, and phosphomolybdic acid with a molybdenum-phosphorus ratio of 18 to 2, both available as the sodium salts. There are innumerable other possibilities, because at least 25 different elements function as hetero atoms in distinct heteropolymolybdate anions (*5*). Any one of these high-weight anions is a potential precipitating agent for basic organic dyes to give new color lakes and toners.

Valuable dyes with great affinity for natural or artificial textile fibers, particularly casein, can be produced from molybdenum oxide and the tetrasulfonic derivatives of phthalocyanine dyes, or by the reaction of the monosulfonic derivative of an aromatic compound such as phthalic anhydride with the metallic oxide in the presence of urea (*27*). Metallized diazo dyes for animal fibers have also been made through the chelating action of molybdenum. These products, dark-colored powders of varied shades of brown, are water-soluble (*8*).

Solutions of molybdates have also been found to give a strong, yellow precipitate with a salicylhydroxamic acid; the product dissolves readily in alcohol. This colored complex possibly contains quinquevalent molybdenum in the anion, the probable formula for which is $MoO_2C_7H_5O_3N$. Similar colorations have been observed with benzyhydroxamic acid. These colors have been suggested as tools for the colorimetric estimation of vanadium in the presence of molybdenum and uranium (*2*).

Other complexes in the Mo—N—C system are those formed by molybdenum hexacarbonyl or molybdenum pentachloride, and pyridine. Satisfactory characterization of the sexivalent coordination substitution derivatives of molybdenum hexacarbonyl has been accomplished by Hieber on the following compounds, which he synthesized (*14*):

$Mo(CO)_3$·3 pyridine
$Mo(CO_4$·*o*-phenanthroline
$Mo(CO)_3$·pyridine, *o*-phenanthroline

Although mercaptans did not react with molybdenum hexacarbonyl to form a sulfur-bonded derivative, thiophenol reacted with molybdenum tricarbonyl pyridine to form molybdenum dicarbonyl thiophenate pyridine (*15*).

Molybdenum-Oxygen-Carbon System. Only one group of compounds containing the molybdate anion nucleus—that of the complexes with oxalic acid—has been systematically studied. The oxalate derivatives of molybdenum(VI) are most easily prepared by dissolving molybdic oxide in an aqueous solution of an oxalate (*20*). The equimolar complex, $H_2{}^{+2}[MoO_3(C_2O_4)]^{-2}$, can undergo photochemical autoreduction-oxidation in air with formation of molybdenum blue, a molybdenum oxide hydrate of valence intermediate between molybdenum(V) and molybdenum(VI). In an early German patent, a photographic application of this photochemical reactivity of the oxalate is described (*19*). Alkali and ammonium salts of this complex appear to be more stable forms than the acid.

The oxalate derivatives of molybdenum(V) are stable in air. Prepared by the reduction of an aqueous solution of ammonium molybdate and the oxalate salt (*1*), these are red crystalline complexes to which the following structure has been assigned: $M^+[MoO_2(C_2O_4)]^-$ ($M^+ = H^+, K^+, NH_4{}^+, \frac{1}{2}Ba^{+2}$, pyridinium).

The reaction of electrolytically formed molybdenum trihydroxide with oxalic acid in the absence of air is reported to form molybdenum(III) oxalates (*38*). When heated in air, these compounds decompose to oxalates of isopolymolybdic acids. Some

less well characterized molybdenum(III) derivatives of sodium salicylate and disodium phthalate have been prepared by reaction with M_2MoCl_5 or M_3MoCl_6 ($M^+ = NH_4^+$, K^+) (*4*). Syntheses of poorly characterized molybdate complexes from *o*-hydroxyphenols, such as catechol, or pyrogallol (*10*), have been reported. The catechol derivatives of ammonium dithiomolybdate have also been described (*11*).

Amino- and hydroxy-substituted aromatic compounds form complexes with soluble molybdates to yield permanent red-brown colors in dyeing animal fibers. The dyeing process is carried out by soaking fur fibers in a 4% aqueous solution of pyrogallol, followed by a second soaking in an ammoniacal solution of molybdic acid (*18*). Spirit or oil varnishes are converted to stains in a like manner.

A new metal coating process in which a soluble phosphate and a complex between a soluble molybdate and a polyhydric phenol are the featured ingredients has been applied commercially. Used to pretreat iron and steel parts prior to painting or finishing in some other manner, it prevents cracking and flaking of the finish if the part must be fabricated after painting. This result is attributed to a dense and amorphous phosphate coating which will withstand considerable working (*32*).

Quebracho is the most commonly used polyhydric phenol in this coating process, but sumac tannin, catechol, resorcinol, hydroquinone, pyrogallol, pyrogallic acid, gallic acid, and phloroglucinol have also been used (*9*). Coating solutions containing 2 ounces of the complex mixtures per gallon produce hard, continuous phosphate coatings averaging 100 mg. per square foot of ferrous metal surface.

The characterization of covalent chelate derivatives has been limited to molybdenum acetylacetonates. Yellow, solid molybdenum (VI) acetylacetonate has been prepared by a condensation reaction of acetylacetone with molybdic oxide (*26*). This compound must be isolated at reduced temperatures in order to prevent decomposition to molybdenum blue (*25*).

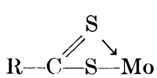
Using Wardlaw's molybdenyl monochloride hydrate (*39*), Morgan prepared a water-soluble molybdenum(III) acetylacetonate, which was readily air-oxidized to a green molybdenum(V) acetylacetonate, soluble in both water and organic solvents. Data have recently been obtained for a complex with ethylenediamine tetraacetate. There are two molybdenum atoms per ligand of ethylenediamine tetraacetate, a structure which appears unique among such complexes (*28*).

Other compounds, presumably chelates, are the benzoinoxime and 8-quinolinol complexes which are used for precipitation of molybdenum from aqueous acid molybdate solutions.

Molybdenum and acetyl- or benzoylacetone are claimed to form colored chelates, which, when added to a monomer in a polymerization system, give colored polymers (*6*).

Molybdenum-Sulfur-Carbon System. Because Mo—S bonds are less ionic than Mo—O bonds and sulfur has a greater covalent coordinating tendency than oxygen, organic sulfur complexes of molybdenum should be more soluble in organic media and less reactive toward the common ionized reagents.

Malatesta has carried out a systematic study of molybdenum xanthates and dithiocarbamates (*24*), both of which are probably stabilized by the following basic chelate group:



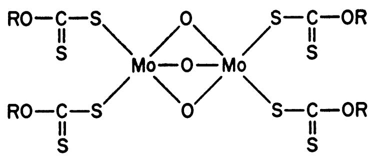
R=alkoxy or dialkylamino

These compounds are prepared by reduction of an aqueous solution of the molybdate and the alkali metal salt of the dithioacid. Recent work has demonstrated that only the molybdenum(V) ion forms the xanthate (*29*). These compounds are soluble in organic solvents, insoluble in water, and undergo oxidative decomposition upon standing. The dialkyldithiocarbamates are similar in structure to the xanthates, but are less

well defined, because of tendencies to undergo polymerization. They are more stable than the xanthates and less soluble in organic solvents.

The use of natural molybdenum disulfide as a solid film lubricant additive to chassis greases has been described (*36*). Other lubricating applications in the automotive field await the development of stable dispersions of molybdenum disulfide in oil media. One approach to this problem has been to synthesize oil-soluble molybdenum-sulfur organic compounds which appear to decompose as the friction-induced temperature increases. A molybdenum sulfide film is reported to be continuously deposited on the metal surfaces. Such organic compounds could be added to extreme-pressure and hypoid gear oils to improve lubricity and to prevent metal-to-metal contact at friction interfaces.

Hugel has reported the seizing times for varying applied loads on a 4-ball testing machine, using an SAE 30 oil with 2% of a molybdenum decyl xanthate added. This decyl xanthate is of the general formula:



where R may be hexyl, octyl, decyl, or dodecyl. Of these compounds, the decyl xanthate was found to have optimum solubility and stability (*16*).

Hugel's data indicate that this compound as a lubricant additive prevents seizing under extreme pressure conditions, reduces wear, and maintains a well-lubricated motion. Additional work is in progress with the xanthate and thiocarbamates to improve the stability or shelf life of these additives.

Similar lubricating applications are proposed for the alkyl-substituted ammonium salts of tetrathiomolybdic acid, $(RNH_3)_2MoS_4$. These salts are prepared by reaction of the amine hydrochloride with ammonium or alkali metal tetrathiomolybdate in aqueous solution:

$$2RNH_2 \cdot HCl + Na_2MoS_4 \rightarrow (RNH_3)_2MoS_4 + 2NaCl$$

These compounds apparently have some solubility in solvents such as polyalkylene glycols (Ucon fluids) and in fatty acid oils, but are insoluble in petroleum solvents and can be dissolved in water only with difficulty (*3*).

Chelates as Catalyst Raw Materials. Several patents have recently claimed the use of organomolybdenum compounds as raw materials for supported catalysts, in order to avoid the usual evolution of ammonia vapors from ammonium molybdate by impregnating a catalyst carrier with molybdenum oxalate in aqueous solution (*33*). Another application proposes the use of monoethylammonium tetrathiomolybdate (probably an ethyl-substituted ammonium salt of tetrathiomolybdic acid, made as described above) as a hydrogenation-dehydrogenation catalyst material. The carrier coating, after calcining at 300°C., is reported to be molybdenum trisulfide. Only after nitrogen treatment at 440°C. are coatings of crystalline molybdenum disulfide obtained (*37*).

Recognition that subsexivalent molybdenum is the active catalyst in a variety of chemical reactions may lead to further utilization of the organic complexes as molybdenum catalyst raw materials. The multivalent forms (+3 to +6) of the oxalate complexes make these likely choices for such materials. Solubility limitations of these oxalates, however, direct attention to their use in two types of catalysts: supported catalysts, which require that the molybdenum be in a water-soluble form; and catalysts which are used as insoluble crystals or amorphous gels in vapor or liquid phase reactions.

Because many of the organic complexes now under investigation are oil-soluble, their potential catalytic use in homogeneous hydrocarbon reactions is of great interest. The xanthates and thiocarbamates are also oil-soluble and offer a means of manufacturing molybdenum sulfide catalysts, both supported and unsupported. New molybdenum esters have a similar potential in catalytic applications.

Molybdenum Esters

Over 50 years ago, Rosenheim described the existence of a dimethyl ester of molybdic acid (*34*), prepared by adding molybdic oxide dihyrate to methanol. Critical present-day re-examination of this claim strongly suggests that an alcoholate and not an ester was formed.

Rosenheim (*35*) has more recently described the only known simple ester type compound, triphenoxymolybdenum dichloride, $MoCl_2(OC_6H_5)_3$. It was prepared by the reaction of 1 mole of molybdenum pentachloride with 4 moles of phenol in carbon disulfide, giving a dark, red-purple, crystalline solid. This compound is soluble in carbon disulfide and benzene, and is reported to be hydrolytically stable, although such hydrolytic stability has not been confirmed. The phenoxy compound is probably stabilized by double bond resonance involving the benzene ring. It is not known under what conditions molybdenum alkoxides can be synthesized and whether they exist in a stable form.

Other cresylic acids, derivatives of salicylic acid, catechol, and 2-hydroxy-*m*-toluic acid, form similar esters which complex with organic and inorganic bases.

Organomolybdenum Compounds

Cotton has recently reviewed the subject of alkyl and aryl derivatives of the transition metals (*7*). For the purpose of his paper, he defined organometallic compounds exclusively in terms of alkyl and aryl derivatives of a metal. In it, three other parallel classes of metal-carbon bonded compounds are briefly discussed:

1. Carbonyls, cyanides, and cyanide complexes, isocyanides, and acetylides
2. Olefinic or acetylenic compounds
3. Cyclopentadienyl derivatives

The only alkyl and aryl derivatives of molybdenum reported in that review were the phenylmolybdenum compounds of Hein, about which there has been much dispute. Information concerning classes 1 and 3 has recently been made available.

Molybdenum carbonyl is regarded as the parent compound for the cyclopentadienyls and can be considered an organometallic, as can its cyclopentadienyl derivatives, in this paper. The pronounced shortening of the Mo—C bond distance relative to that expected from the sum of covalent radii indicates extensive π-bonding in the carbonyl. On the other hand, the Mo—C bond force constant is in the exact range to be expected for single electron-pair bonds between molybdenum and carbon.

Molybdenum Hexacarbonyl. Molybdenum hexacarbonyl is the most stable compound among the Mo—C bonded classes, because of octahedral, electron-pair coordination, and covalent bonding. It is relatively simply made in good yields and thus lends itself readily to commercial application.

The best preparation technique to date is that which was described by Kocheshkov (*21*), as modified by the Bell Laboratories. The reaction is carried out in an autoclave using anhydrous molybdenum pentachloride dissolved in ether. Finely divided zinc is used as both a metallic catalyst and a reducing agent for the chloride. Pressures of carbon monoxide vary from 600 to 1100 p.s.i. with an average pressure of about 800 p.s.i. Autoclave temperatures have varied widely around room temperature, because of the exothermic nature of the reaction and of the variations in the cooling technique.

A recent patent suggests the use of an aluminum alloy powder, containing

50% copper, 45% aluminum, and 5% zinc, instead of all zinc. With this alloy, a 90% yield of the carbonyl is obtained at 100°C. and 1500 p.s.i. in a reaction time of 3 hours (*17*).

Table I. Properties of Molybdenum Hexacarbonyl

Formula	$Mo(CO)_6$	
Molecular weight	264.01	
Appearance	White crystals, diamagnetic	
Melting point, °C.	Volatile, decomposes below 150° C.	
Specific gravity	1.96	
Solubility		
Water	Insoluble	
Ether at 30° C.	2.5 wt.%	
JP4, jet fuel	30° C./10.99 g./l.;	50° C. 18.30 g./l.
JP5, jet fuel	7.78	17.90
MIL 7808, lube oil	3.96	11.95
Vapor pressure		
80° to 150° C.	$\log_{10} p = 11.406 - 3654/T$	
0° to 50° C.	$\log_{10} p = 11.795 - 3800/T$ (p in mm. of mercury, T in °K.)	
Stability		
Water	Stable	
Air	Stable	
Acids	Stable	
Strong basic solutions	Decomposes	
Bromine vapor	Decomposes, forms $MoBr_4$	
Heats of combustion		
Q_v	507.58 kcal./mole	
Q_p	506.69	
Heat of formation		
Q_p at 25° C. calcd.	233.12	
Heat capacity	$0.22804 + 0.0_4848t - 0.0_51264t^2$	
Specific heat	$0.22974 + 0.0_32202t - 0.05379t^2$ (c_p values are per unit weight of molybdenum contained and apply to temperature range 20° to 78° C.)	

The physical properties of the carbonyl compound are shown in Table I. Its apparent lack of toxicity may be due in large measure to its low vapor pressure at room temperature, in contrast to the other carbonyls which may have appreciable vapor pressure even at room temperature and hence are very poisonous if inhaled.

Molybdenum carbonyl may be thermally decomposed at low temperatures in a variety of atmospheres to yield films of molybdenum metal, molybdenum carbide, and molybdenum sulfides and oxides. This property makes molybdenum carbonyl interesting as a material in many pyrolytic plating processes.

Coatings on metallic and nonmetallic—for example, ceramic—particles have wide commercial implications. Probably the most important of the products obtained thus far are the alloys with carbon and the carbides. Coherent and adherent coatings of the carbides on a base metal have been made by adjusting the plating condition to give any value of carbon content from zero to about 35 atomic %. The hardness depends primarily on this carbon content in the plate, some coatings being harder than sapphire. New carbides of molybdenum and alloys supersaturated with carbon have also been produced.

Plating can be carried out at temperatures as low as 150°C. and thus, in the presence of other substances like carbon monoxide, hydrogen sulfide, and water reactions occur which could not be produced in another way. Equilibrium data relating temperature and gas composition for the preparation of plate compositions containing given quantities of carbon, sulfur, or oxygen have been presented by Lander and Germer (*22*).

Pure molybdenum coatings may have application in electronic or electrical devices, in the field of high temperatures, and in catalytic applications. The hard alloys with carbon, and the carbides, may provide good wearing surfaces for bearings, dies, rolls, gages, and other tools. Molybdenum sulfide, formed via vapor plating, may be useful as a lubricating film, as a semiconductor, and as a catalyst on a variety of nonmetallic supports.

Aryl Isocyanide Derivatives

Malatesta (*25*) has prepared molybdenum hexaaryl isocyanides, $Mo(CNR)_6$, in low yields by reaction of aryl isocyanides with molybdenum trichloride in alcohol. These compounds undergo slow decomposition in air.

π—$C_5H_5Mo(CO)_6$ Moπ—C_5H_5

Molybdenum hexacarbonyl reacts with cyclopentadiene or with sodiumcyclopentadiene in tetrahydrofuran to give a series of cyclopentadienylmolybdenum compounds, of which ferrocene is the prototype. The molybdenum atom is bonded to the cyclopentadienyl ring by a delocalized and essentially covalent bond. There are no covalent bonds between a particular carbon atom and the molybdenum atoms.

The following series of reactions illustrates the range of stable compounds which have been made in this new class (*30*):

Preparation of Intermediates

$$C_5H_5Na + Mo(CO)_6 \rightarrow C_5H_5Mo(CO)_3Na + 3CO$$

$$C_5H_5Mo(CO)_3Na + HOAc \rightarrow C_5H_5Mo(CO)_3H + NaOAc$$

Typical Reactions

$$2C_5H_5Mo(CO)_3H + Air \rightarrow C_5H_5Mo(CO)_6MoC_5H_5 + H_2O$$

$$C_5H_5Mo(CO)_3H + CCl_4 \rightarrow C_5H_5Mo(CO)_3Cl + CHCl_3$$

$$C_5H_5Mo(CO)_3Na + CH_3I \rightarrow C_5H_5Mo(CO)_3CH_3 + NaI$$

The structure of biscyclopentadienyl carbonyl, π—C_5H_5Mo—$(CO)_6Mo\pi$—C_5H_5, has been the subject of much discussion in recent months. While it was initially believed that it was essentially a "triple-decker sandwich," recent x-ray diffraction studies at the Massachusetts Institute of Technology show that the molecule is a dimer of a cyclopentadienyl molybdenum tricarbonyl. There are no carbonyl bridges to form a supersandwich and the molecule is not linear (*41*).

Alkyl Cyclopentadienyl Derivatives

From the π—cyclopentadienyl molybdenum tricarbonyl hydride, a number of compounds with a metal-to-carbon sigma bond have been prepared as indicated by the above series of reactions (*31*). The following alkyl derivatives were prepared by reacting alkyl halides with π—$C_5H_5MO(CO)_3Na$:

$$\pi\text{-}C_5H_5Mo(CO)_3CH_3$$

$$\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$$

$$\pi\text{-}C_5H_5Mo(CO)_3\ \text{iso}\ C_3H_7$$

All of these compounds are diamagnetic and are readily soluble in petroleum ether (30° to 60°C.) and in the usual organic solvents. They sublime easily in high vacuum at temperatures from 25° to 50°C. and have a noticeable camphoraceous odor. In organic solvents, all the compounds are slowly decomposed by air.

The stability of these compounds is inversely proportional to the length of the carbon chain in the alkyl group. The methyl compound begins to decompose in air after a few days and upon heating in vacuum at 110°C. The ethyl compound is noticeably less stable and the isopropyl compound even less stable.

The compounds are all yellow and are soluble in water and unaffected by it. They are attacked by acids and bases, but do not form cations. Halogens react to form the alkyl halides and the π—cyclopentadienyltricarbonyl halides.

Cyclopentadienyl Carbonyl Hydride

A yield of $C_5H_5Mo(CO)_3H$ of 90% based on molybdenum hexacarbonyl was obtained by the reaction shown above. The hydride sublimes at 10^{-2} mm. of mercury and 50°C. In nonpolar solvents, such as petroleum ether, the hydride is decomposed to a black mass by air. However, in polar solvents, such as tetrahydrofuran, smooth oxidation to π–$C_5H_5MO(CO)_6MO\pi$–C_5H_5 occurs (*31*).

Reaction of the hydride in an excess of carbon tetrachloride gives π–$C_5H_5Mo(CO)_3Cl$ and $CHCl_3$ at 25°C. The chloride exists as orange-red crystals, decomposing at 145°C. without melting. It is only slightly soluble in petroleum, but is soluble in polar organic solvents without decomposition. The bromide and iodide have also been prepared from the hydride. Red crystals of these halides melt at 150–1°C. and 134–5°C., respectively.

The compound, π–$C_5H_5Mo(CO)_2NO$, can be made by direct action of nitric oxide on the hydride in an organic solvent. This compound forms stable orange crystals, melting at 85.2–5.7°C. and is readily soluble in organic solvents without decomposition.

Dibenzene Molybdenum

The other outstanding development in organometallic research is the synthesis and characterization of dibenzene compounds of chromium, molybdenum, and tungsten by Fischer (*12*). This unique discovery has cleared up the perplexing question of the nature of the supposed phenylchromium and molybdenum compounds of Hein (*13*). Dibenzenemolybdenum (as well as chromium and tungsten) has been found to possess a hexagonal, prismatic, centrosymmetric structure.

Dibenzene molybdenum is synthesized from molybdenum pentachloride first as an aqueous soluble cation (unstable in air), which is then reduced to a compound that is very unstable in air, is soluble in organic solvents, and is also neutral. The formation of the cation is carried out in a bomb heated to 150°C. The following equation shows the synthesis:

$$3MoCl_5 + 4Al + 6C_6H_6 \xrightarrow[150^\circ C.]{AlCl_3} 3Mo(C_6H_6)_2 + AlCl_4 + 3AlCl_3$$

After hydrolysis of the complex, the cation is reduced by a new reducing agent, $(NH_2)_2C(SO_2K)_2$, diaminomethane disulfonium potassium. As the neutral dibenzene molybdenum is unstable in air, care must be taken to extract and sublime it under oxygen-free conditions. Dibenzene molybdenum thermally decomposes at 100°C. to give a metal mirror.

Future Objectives

Research and development on organomolybdenum compounds are expanding at a pace characteristic of the entire field of metal chemicals. The above discussion has been devoted to the chelates, esters, and organometallic compounds of molybdenum. Only the chelates have found extensive commercial utilization as brilliantly colored organic pigments and as metal coatings. A more complete summary of uses and potential uses for these complexes is presented in Table II. Catalysts and new pigments appear to hold considerable promise for future utilization of organomolybdenum compounds.

Preparation of the chelate derivatives depends largely upon the availability of soluble compounds of molybdenum. Molybdic oxide and sodium molybdate have been generally used as starting materials for the chelates. Other simple, isopoly salts and heteropolymolybdates are now becoming familiar to organic chemists. Molybdenum pentachloride is a convenient starting material for the known ester, triphenoxy molybdenum dichloride and molybdenum hexacarbonyl for the organometallics.

Table II. Uses for Molybdenum Organics

Type	Bonding	Present Commercial Uses	Potential Uses
Chelates	Mo—N—C	PMA and PMTA color lakes and toners for printing inks, tints, water colors, show card inks, wax crayons, colored paper, and enamels for children's toys	New toners from other heteropoly acids Casein dyes from phthalocyanine derivatives Metallized diazo dyes; colorimetric analyses
	Mo—O—C	Metal coatings using phenolic complex	Catalysts
	Mo—S—C		Lubricants
Esters	$MoCl_2(OC_6H_5)_3$		Catalysts
Organometallics	$Mo(CO)_6$		Vapor plating Catalysts
	$C_5H_5Mo(CO)_3H$		Catalysts Ion exchange resins New plastics Modified resins

Organomolybdenum compounds, derived from molybdenum hexacarbonyl, are receiving systematic attention in industrial and academic laboratories at the present time. Molybdenum carbonyl, considered as the parent of the known organometallics, has proved practical for the vapor plating of metallic molybdenum or intermetallic films on metal or ceramic surfaces. Vapor plating may be a satisfactory alternative to electroplating, which has never proved completely feasible for molybdenum.

Cyclopentadienyl derivatives are the subject of intense, fundamental study. Potential uses for these organometallics are also suggested in Table II. Application research will follow the synthesis and characterization of any of these stable derivatives.

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The Amine Method for Preparing Ferrocene

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Ferrocene can be prepared on a laboratory or large-scale basis by the reaction of ferrous chloride and sodium cyclopentadienide in an amine solvent. The basicity of the latter is an important factor in the yield of ferrocene obtained. Other factors affecting the course of the reaction as well as the yield are discussed.

A recent review article by Pauson (*6*) describes the preparation, properties, and reactions of ferrocene [or bis(cyclopentadienyl)iron] and related compounds. Several reactions are listed as possible methods for preparing ferrocene:

1. Cyclopentadiene and iron powder at high temperature (*5*).
2. Cyclopentadienylmagnesium halide with ferric halide (*4*).
3. Cyclopentadienylmagnesium halide with ferric acetylacetonate (*7,11*).
4. An alkali metal cyclopentadienide with ferrous or ferric halides (*8,9*).
5. An alkali metal cyclopentadienide with iron hexammine salts (*2,3*).
6. Cyclopentadiene with iron halide in an amine solvent (*1,10*).

The Linde Laboratories, early in their work on organometallic compounds, developed two of these methods for the preparation of ferrocene. The reaction of iron(II) chloride with sodium cyclopentadienide in ethylene glycol dimethyl ether (DMC) solvent:

$$FeCl_2 + 2NaC_5H_5 \xrightarrow{DMC} (C_5H_5)_2Fe + 2NaCl \qquad (1)$$

and the reaction of cyclopentadiene with iron halides in diethylamine solvent:

$$2C_5H_6 + FeX_2 + 2R_3N \rightarrow (C_5H_5)_2Fe + 2R_3N \cdot HX \qquad (2)$$

These two methods appear to be the most attractive possibilities for large-scale preparation of ferrocene. The second method was later published by Wilkinson and coworkers as a laboratory preparation of ferrocene (*1*), even though their first attempts gave very low yields. This paper shows the applicability of the amine method for the preparation of ferrocene on either a laboratory or production scale.

The reaction given in Equation 2 gives excellent yields of ferrocene, 85 to 90% of theory, when a highly basic amine is used. The success of this reaction apparently depends upon the formation of an intermediate according to Equation 3:

$$C_5H_6 + R_3N \xrightarrow[\text{Amine}]{\text{XS}} [R_3NHC_5H_5] \rightarrow R_3NH^+ + C_5H_5^- \qquad (3)$$

Table I shows the results of using amines of varying basicities in this reaction. The data were taken from experiments in which stoichiometric amounts of iron(II) halide and cyclopentadiene were used. The amine was employed in considerable excess as both a reactant and a solvent for the reaction. Since the iron halide was prepared in ethylene glycol dimethyl ether, this was used as a cosolvent. Iron(II) chloride was prepared by the reaction of anhydrous iron(III) chloride with iron powder in ethylene

Table I. Effect of Amine Structure

Amine	% Yield of Ferrocene	Log K_A[a]
Diethylamine	85	11.0
Piperidine	69	11.3
n-Propylamine	38	—
Di-*n*-propylamine	29	—
Triethylamine	20	10.8
n-Butylamine	7	10.7
Ammonia	3	9.3
1,6-Hexanediamine	<1	—
Ethylenediamine	Trace	~10
Pyridine	None	5.4
Morpholine	—	8.7

[a] $\text{Log } K_A = \log \frac{(AH_+)}{(A)(H_+)}$.

glycol dimethyl ether. Iron(II) bromide was prepared by the direct bromination of iron powder with bromine in ethylene glycol dimethyl ether. Both of these reactions proceed smoothly and rapidly at or near room temperature.

It may be seen from the table that the basicity of the amine is very important in producing satisfactory yields of ferrocene, although this may not be the only critical factor. The two best amines, diethylamine and piperidine, are the most basic, having log K_A values of 11.0 or higher. With amines of lower basicity the yield of ferrocene decreased approximately in the order of decreasing log K_A. An apparent anomaly in the case of ethylenediamine may be due to the formation of strong complexes with the ferrous ion, thus preventing the reaction of the ferrous halide.

Product yields may be increased over those shown in Table I even in the presence of amines of intermediate basicity by increasing the amounts of cyclopentadiene over those required by Equation 2 (Table II). The increase in yield is approximately the same as the increase in molar ratio of cyclopentadiene to metal halide.

Table II. Effect of Excess Cyclopentadiene

Amine	Molar Ratio CPD[a] to FeX_2	% Yield Ferrocene Based on FeX_2
Triethylamine	2 to 1	20
	8 to 1	72
n-Butylamine	2 to 1	7
	8 to 1	32

[a] CPD = cyclopentadiene.

The results described thus far were obtained from experiments in which a large excess of the amine was used. Table III gives the results of experiments in which stoichiometric amounts of the amine were used in the presence of an inert solvent. With either benzene or DMC as the solvent the yields were markedly decreased.

Table III. Effect of Excess Amine

Amine	Molar Ratio Amine to CPD[a]	% Yield of Ferrocene
Diethylamine	1 to 1 (in benzene)	15
	Large (amine as solvent)	75–85
Piperidine	1 to 1 (in DMC)	19
	Large (amine as solvent)	69

[a] CPD = cyclopentadiene.

Table IV shows the variation in yields when various iron salts were employed.

Table IV. Product Yield from Various Iron Salts

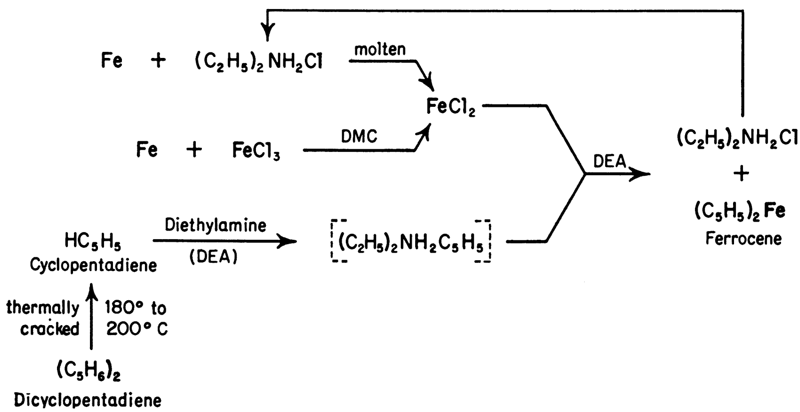
Iron Salt[a]	% Yield of Ferrocene
$FeCl_2$	75–85
$FeBr_2$	85
$FeSO_4$	0
$FeCl_2 \cdot 4H_2O$	0

[a] All reactions in diethylamine-DMC.

There was no marked difference between iron(II) chloride prepared by reduction of iron(III) chloride with iron powder and iron(II) bromide prepared by the bromination of iron. The bromide gave slightly better results, probably because of the increased solubility of the bromide in the solvent. Iron(II) sulfate and iron(II) chloride tetrahydrate failed to produce ferrocene. The results with the hydrated salt show a point that was confirmed in other experiments; it is essential that all materials be thoroughly dried. In these laboratories the amines were dried by passing them through a column packed with Linde 4A Molecular Sieve. DMC was dried, and its peroxides were also removed, by the Linde 13X Molecular Sieve.

As a laboratory preparation, commercial anhydrous iron(III) chloride may be used directly with cyclopentadiene in diethylamine solvent. Yields of about 85% may be obtained, based on iron. In this case it is necessary to use a 3 to 1 molar ratio of cyclopentadiene to iron, because 1 equivalent of cyclopentadiene is used in the reduction of iron(III) chloride to the iron(II) state. This is a very convenient laboratory preparation, because it gives a high yield of product from a short, one-step process. On a large scale it is less attractive because it requires 50% more cyclopentadiene.

For a commercial process, there is an important modification in which iron powder may be used as a raw material. The by-product of the reaction of iron(II) chloride with cyclopentadiene is the amine hydrochloride. This amine hydrochloride may be recovered in usable form as the neutral amine by treating it with iron powder. When diethylamine hydrochloride is heated with iron powder, hydrogen is evolved and iron(II) chloride and diethylamine are formed. This iron(II) chloride can then be used in the regular process to form ferrocene. Thus, the diethylamine hydrochloride may be recycled, so that the only raw material requirements are iron metal and cyclopentadiene, with hydrogen as a by-product. This over-all process is outlined in the following simplified flow diagram.



It may be concluded that the amine method affords a convenient and cheap process for the preparation of ferrocene on either a laboratory scale or production scale.

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